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Chapter 2

Cold Plasma Produced Catalytic Materials

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Abstract

The cold plasma techniques are widely applied to create new materials possessing unique properties, which cannot be prepared by any other methods. Among the many interesting substances produced with the participation of cold plasma, a special place is occupied by materials with catalytic properties. The chapter gives a brief review of various cold plasma methods used for the preparation of catalytic materials – from the plasma modification of conventional catalysts via plasma-enhanced classical synthesis of catalysts to the advanced thin catalytic films fabricated by plasma sputtering processes but primarily by plasma deposition from metalorganic precursors (PECVD). Recently, the catalytic films have attracted considerable attention due to the possibility of depositing them as very thin coatings on virtually all supports without any change in their geometry. Such coatings open the way for new reactor designs, so-called structured reactors, designated for various chemical processes. They can also be used as catalytic deposit on the surface of electrodes for fuel cells and photoelectrodes for water splitting processes. Recent developments in this field and further prospects for thin catalytic films are discussed, all the more so because it is one of the main areas of research in our department.

Keywords: Catalysts, plasma treatment, PECVD, structured reactors, fuel cells, water splitting

1. Introduction

For a long time, plasma techniques have been used in the creation of new materials possessing unique properties, which cannot be fabricated by other methods. A particularly important technique, giving plenty of possibilities, is the plasma deposition of entirely new, advanced materials in the form of solid coatings having unusual molecular structure and sophisticated nanomorphology. The plasma processes can also be used to modify conventional materials through treating them during or after "classical" synthesis, which generally leads to new

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substances with disparate properties, often more suitable than those of the unmodified materials.

Among the many interesting products fabricated by plasma techniques, materials with catalytic properties occupy a special place. There exist a lot of catalytic reactions, for example, combustion of organic volatile compounds, CO_2 methanation, Fischer–Tropsch synthesis, water photo-splitting, fuel cell electrode processes, and many others, which challenge chemists all over the world to seek better catalysts or more effective catalyst preparation methods. It seems that the plasma techniques pave the way for novel solutions in this field.

In general, plasma techniques used in the preparation of catalysts can be categorized into one of two groups depending on the plasma type: thermal (equilibrium) plasma and cold (none-quilibrium) plasma [1—3]. The thermal plasma is employed in the preparation process mainly through plasma spraying of catalytically active compounds [4—6] as well as washcoats [7] on various carriers and usually in the form of thicker coatings (>> 1 μm). However, it can also be utilized for the synthesis of ultrafine catalysts whose particle diameters are in the range from a few to a few tens of nanometers and specific area is highly developed [2, 8]. Lately, graphene nanoflakes for catalytic applications have been produced by thermal plasma [9, 10]. Also, this plasma technique is used to recover and regenerate the spent conventional catalysts [11, 12]. Very recently, a more sophisticated method of the catalyst preparation employing thermal plasma has been discovered. For example, very small Ni particles (<100 nm) attached to MgO nano-rods of 10–20 nm in diameter were fabricated by an RF thermal plasma flame, into which a solid precursor consisting of Ni and MgO powders (~5 μm and ~100 nm, respectively) was injected [13]. In turn, Nehe et al. [14] proposed a new promising technique of depositing nanostructured films, namely the solution precursor plasma spray (SPPS) technique. This method was employed to the deposition of $CuO–ZnO–Al_2O_3$ layers that were later successfully used to catalyze the methanol reforming for the production of hydrogen (H_2) gas.

On the other hand, the cold plasma, in which all processes proceed at much lower temperatures (up to a few hundred degrees centigrade) than those in the thermal plasma (much higher than 1273 K), is a very promising tool for the preparation of catalytic materials [1-3, 15]. Recently, these materials have attracted considerable attention due to the possibility of depositing them as very thin coatings (<< 1 μm) on virtually all supports without any change in their geometry. Such coatings open the way for new reactor designs, so-called structured reactors, for various chemical catalytic processes [16]. They can also be used as catalytic deposits on the surface of fuel cell electrodes without practically any changes in their electrical conductivity and gas permeability. Further advancement is also expected with regard to new sophisticated thin films for photocatalytic splitting of water molecules and efficient production of hydrogen [17]. Apart from the thin catalytic coating deposition, the cold plasma is also utilized in preparations of conventional catalysts, through both plasma enhanced "classical" synthesis and plasma modification of as-prepared "conventional" catalysts [2, 15].

The cold plasma preparation of catalytic films, carried out by plasma polymerization processes from organometallic complexes as precursors, and study of their properties are the main research fields in our laboratory. However, for the sake of completeness, cold plasma involve-

ments in the preparation of "conventional" catalysts as well as sputtering processes are also discussed in this chapter.

2. Cold plasma for "conventional" catalysts

There are two ways of application of plasma to the conventional production of catalysts: plasma treatment during formation of catalyst and plasma modification of catalysts that have been already conventionally formed for commercial application. The first way can be used to replace the thermal calcination or reduction of a catalyst, to modify its structure, for example, its dispersion and particle sizes, as well as to immobilize catalytic species on supports. Due to chemical treatment with active plasma, catalysts prepared in this way are usually very different from those synthesized only conventionally. Evident changes in the properties of a conventional catalyst can also be achieved by plasma treatment of its final form. Very often, the activity and selectivity of such a catalyst can be significantly improved this way [3, 15 and references therein].

2.1. Plasma-enhanced preparation of "conventional" catalysts

The results published by Chen et al. in 2004 can serve as the classic example of a comparison between a conventional catalyst and such a catalyst prepared by applying the plasma technique [18]. The catalyst was composed of Pd and α-Al_2O_3 and was tested in the selective hydrogenation of acetylene to ethylene. Both procedures of preparation are shown in Figure 1. In the plasma procedure, conventional thermal calcination and reduction processes are replaced with plasma treatment. Apart from the fact that plasma processing is much quicker, cleaner, and easier to control, it was found that the catalyst prepared by the plasma procedure exhibited a significant increase in activity and selectivity, compared with the conventional samples, especially at the lower reaction temperature. Typical results are given in Figure 2, where a drastic difference between the plasma and the conventionally fabricated Pd/α-Al_2O_3 catalysts is evident.

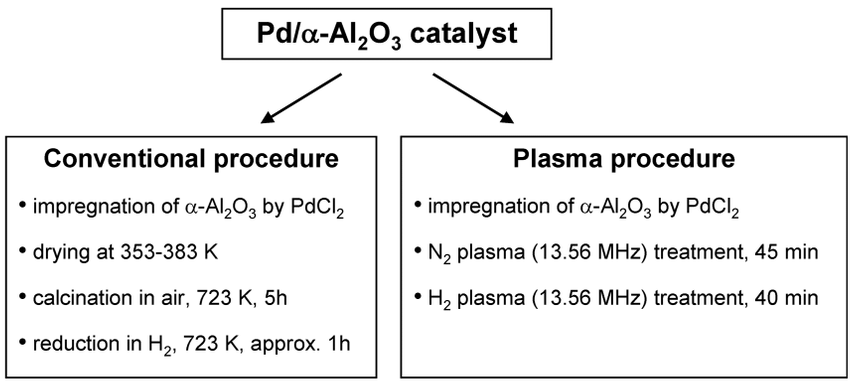


Figure 1. Two ways of preparing the Pd/α-Al_2O_3 catalyst (on the basis of Ref. [18]).

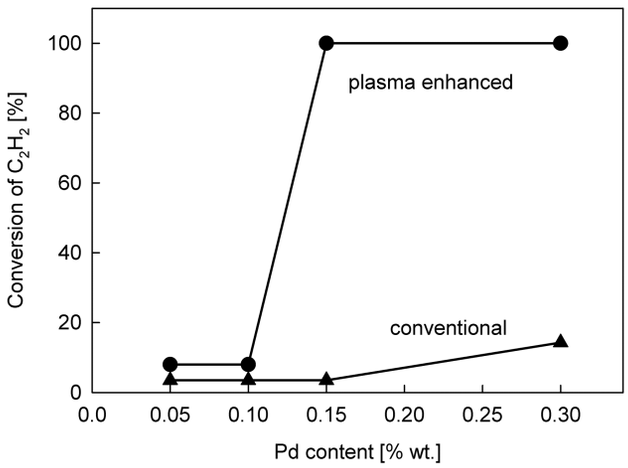


Figure 2. Conversion of C_2H_2 to C_2H_4 versus Pd content for the conventional and plasma-enhanced Pd/α-Al_2O_3 catalysts (on the basis of Ref. [18]).

The investigations simultaneously performed by Liu et al. [19] confirmed that plasma treatment during the fabrication of conventional catalysts is critical to the formation of their structure. They have shown that Ar plasma treatment between the preparation steps of drying after impregnation ($PdCl_2$ solution) and the thermal calcination evidently modifies the structure of palladium catalysts supported by a zeolite (Pd/HZSM-5). An enhanced dispersion of PdO and increase in Brönsted and Lewis acidities, which leads to a remarkable improvement in the catalyst stability, have been observed. It has also been found that combustion of methane (to carbon dioxide and water) over the plasma-treated catalyst is close to 100% efficient at 723 K, but it is only approximately 50% efficient at the same temperature over the catalyst not subjected to plasma treatment. In turn, the investigations performed by Zhu et al. [20] on a Mo-Fe/ HZSM-5 catalyst, tested for the non-oxidative aromatization of methane, have shown that Ar plasma treatment benefits the formation of carbonaceous species associated with the active species of MoC_X and disfavors the coke formation, which in turn leads to deactivation of the catalyst. The crucial role of plasma treatment in the catalyst structure creation was also shown in 2004 by Legard et al. [21]. They used remote hydrogen microwave plasma (2.45 GHz) for the preparation of gold-based metallic catalysts. Unfortunately, gold tends to sinter easily and the conventional reduction of gold performed in hydrogen at high temperatures very often leads to large particles that are not catalytically active. The particles obtained by using plasma are less than 5 nm in size, and are stable during thermal treatment.

In the following years, we could observe a significant growth of interest in employing cold plasma in the conventional catalyst preparation at various stages of this procedure [22–34]. These methods involve plasma initial decomposition of precursors, plasma replacement of calcination and reduction processes, plasma pretreatment of supports, as well as plasma breaking of thin films to form specific nano-sized catalysts. In general, all these plasma processes, in comparison with the entirely conventional method, lead to unusual catalyst structures, built of smaller particles, better dispersion, stronger interaction between the catalyst and the support, and consequently, to much higher activity, enhanced selectivity, and better

stability during a given catalyzed reaction. The anti-carbon deposition and anti-sintering performance are also improved by the plasma treatment. Various types of cold plasma have been tested for this purpose, such as low-pressure glow discharges, atmospheric cold plasma jets, dielectric-barrier discharges, and corona discharges. The plasmas are generated by microwaves (MW), radio frequency (RF, mainly 13.56 MHz), audio frequency (AF, in the range of kHz), alternating current (AC, in the range of Hz), direct current (DC), and even a hot filament, using non-polymerized gases, e.g., Ar, H_2, O_2, N_2, CO_2, NH_3.

Recently, much attention has been paid to the use of dielectric-barrier discharge (DBD) for plasma decomposition of inorganic precursors, such as carbonate mixtures of $CuCO_3$ + $ZnCO_3$ (for CuO–ZnO catalyst) [35] and $NiCO_3$ + $MgCO_3$ (for Ni/MgO catalyst) [36], as well as $Ni(NO_3)_2$ (for Ni catalyst) [37,38] and $Co(NO_3)_2$ (for Co_3O_4 catalyst). This interest stems from the fact that the DBD plasma has turned out to be more reactive than a typical glow discharge. For example, in contrast with the DBD plasma [37], the glow discharge does not lead to the full decomposition of the $Ni(NO_3)_2$ precursor. A specific hydrate is formed during the glow discharge treatment and thermal decomposition has to be carried out before further reactions [39]. The DBD plasma technique also enables simultaneous preparation, in the same process, a support and catalytically active component, as it was done by Hua et al. [36], who treated a powdered mixture of $NiCO_3$ and $MgCO_3$ with the DBD hydrogen plasma to prepare a Ni/MgO catalyst. For comparison, the Ni/MgO catalyst was also prepared conventionally (MgO powder was impregnated with an aqueous solution of $Ni(NO_3)_2$, then calcined at 973 K in air, and finally reduced at 1123 K in hydrogen). An evident difference in the Ni particle sizes between the plasma-fabricated and the conventional catalysts is clearly visible (Figure 3). It has also been found that the plasma-prepared Ni/MgO catalyst exhibits much higher activity and stability in CO_2 reforming of methane.

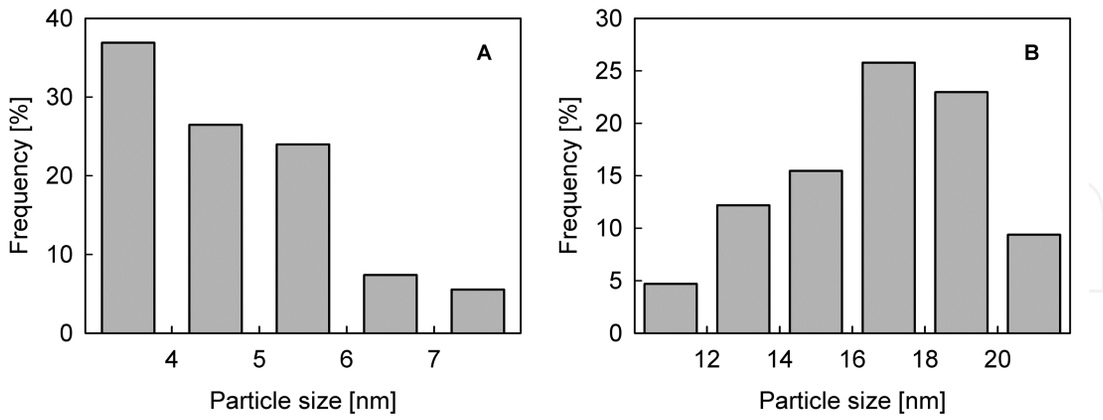


Figure 3. Ni particle size distributions in plasma-treated (A) and conventional (B) Ni/MgO catalysts [36].

It should be emphasized that plasma treatment can generate specific changes in the molecular structure formed during the preparation of a catalyst, which cannot be otherwise obtained. Molecular mechanisms of reactions running with the participation of cold plasma, constituting a complex state containing highly active species, such as ions, electrons,

radicals, and excited molecules, are generally entirely different from "classic" chemical processes that occur during the conventional preparation. For example, Chen et al. [40] showed that plasma treatment (N_2 plasma, 13.56 MHz) favored significant enrichment of Co_3O_4 (cobalt spinel structure) on the surface of a cobalt catalyst prepared by the sol–gel method for combustion of methane, in comparison with only thermal calcination. It is suggested that the bombardment of highly active species on the surface during plasma treatment, inter alia, leads to the breakage of –Si–O–Co– bonds formed in the sol–gel process and creates the Co_3O_4 structure. Such a structure considerably enhances the catalytic performance. Figure 4 presents a comparison between catalysts produced without and with the plasma step. The CH_4 conversion is approximately two times higher in the case of plasma treatment.

The plasma treatment can also be used in more sophisticated processes, where the electronic structure of a material, which is crucial for its photocatalytic activity, will be modified accordingly. Recent studies performed on the so-called black TiO_2 demonstrate that an enhanced solar absorption and excellent photocatalytic activity have been achieved through the introduction of disorder surface layers on the crystalline TiO_2 nanoparticles by plasma hydrogenation. Hydrogen ion bombardment of the particle surface produces large amounts of oxygen vacancies and Ti–H bonds, thereby forming the disorder layer and, consequently, a different electronic structure of the whole nanoparticle. In the surface, tails of localized states occur, which narrows the band gap (to about 2.8 eV from 3.3 eV), but on the other hand, a smaller crystalline core causes widening of its band gap (to about 3.5 eV) [41].

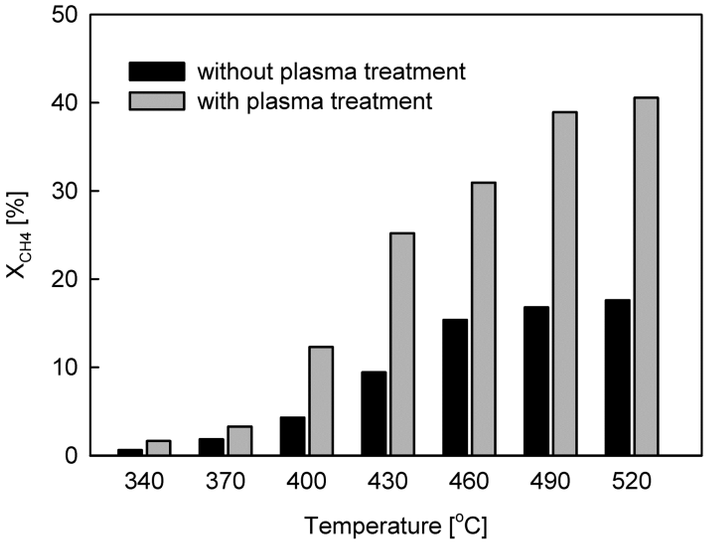


Figure 4. Influence of plasma treatment on catalytic performance [40].

In plasma treatment, a particularly important role is played by electrons that are captured by the treated surface and thus create negative potential with reference to the plasma bulk. Under these conditions, positively charged species possessing high energy bombard the surface

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causing a considerable transformation in its molecular structure practically at room temperature. Besides, the trapped electrons, by their mutual repulsion, elongate or distort bonds, which facilitate dispersion processes [42].

As an example of the plasma decomposition of an inorganic precursor, the process of NiO/Al_2O_3 preparation from nickel nitrate impregnated to Al_2O_3 grains can be given [43]:

$$Ni\left(NO_3\right)_2 + M^* \rightarrow NiO + 2\,NO + {}^3/_2O_2 + M, \quad (1)$$

where M* is an energetic species.

Another example is the plasma formation of a Pd/HZSM-5 catalyst from palladium chloride [42]:

$$PdCl_2 + M^* \rightarrow Pd^{2+} + 2\,Cl^- + M \quad (2)$$

The catalyst can be further reduced by plasma to form pure metal Pd:

$$Pd^{2+} + 2\,e \rightarrow Pd^0 \quad (3)$$

As can be seen, an electron mechanism (involving free electrons) is proposed to explain the plasma reduction. Such a mechanism gives much broader capabilities than typical chemical reduction processes, which usually require high temperatures, resulting in disadvantageous aggregation of metal particles, and are not environmentally friendly. The plasma reduction can be performed at low temperatures in various types of plasma, even in oxygen plasma [44]. However, since the electron mechanism of plasma reduction is governed by electrochemistry and the standard potential of M^{n+}/M^0 pairs determines whether the metal salt can be reduced or not, there are some cases where the plasma reduction process cannot be performed. It has been suggested that the reduction can be observed only when the standard potential is positive. Thus, $PdCl_2$ (Pd^{2+}/Pd^0, E = +0.92 V) can be reduced by plasma treatment (Eq. (3)). On the other hand, $Ni(NO_3)_2$ decomposed into metal oxide (Eq. (1)) cannot be reduced this way (Ni^{2+}/Ni^0, E = −0.25 V) [42].

The plasma treatment is also engaged in appropriate adaptation of catalytic supports through developing their surfaces and increasing the catalyst dispersion. For example, the study focused on Al_2O_3-supported Ni catalysts suggests that the catalysts with Al_2O_3 subjected to plasma treatment before impregnation are relatively easier to reduce and exhibit higher activities under mild reduction conditions [45].

Often, the plasma treatment of supports is utilized to functionalize their surfaces, which enables efficient attachment of the catalysts. Médard et al. [46] used CO_2 plasma to form carboxylic groups on the polyethylene surface, which were able to form pure covalent bonds with metallocene catalysts ($Indene_2MCl_2$, where M = Zr, Ti), then tested them successfully in

styrene polymerization. Lopez et al. [47,48] applied similar treatment to poly(vinylidene fluoride) membranes. The membranes were treated with Ar and then with NH_3 plasma in order to obtain a surface rich in amino groups, which are suitable anchor sites for the immobilization of tungsten-based catalysts. In particular, tungstate ions (WO_2^{4-}), catalyzing the oxidation of secondary amines to nitrones, as well as decatungstate ($W_{10}O_{32}^{4-}$) and phosphotungstate ($W_{12}PO_{40}^{3-}$) ions, which can both be used as catalysts in the degradation of organic pollutants such as phenol, were investigated. The plasma technique was also used to modify the interface between the catalyst nanoparticles and the support. Gold nanoparticles (for hydrogenation of acetylene) were anchored on a SiO_2 support through (3-aminopropyl)triethoxysilane (APTES) molecules that should subsequently be removed. It turned out that O_2 plasma destroyed these molecules giving much higher dispersion of Au nanoparticles (~3 nm) than thermal treatment at 773 K [49].

Among the materials that can be used as catalyst supports in fuel cells, carbon nanotubes (CNTs) and nanofibers (CNFs) have captured increasing attention owing to their high electrical conductivity, large surface-to-volume ratio, and corrosion resistance. However, the non-reactive and hydrophobic nature of the nanocarbons make deposition of catalytically active nanoparticles technically difficult. To overcome this problem, their modification by changing chemical composition of the surface has proven to be efficient. The plasma treatment allows the introduction of appropriate functional groups capable of chemical anchoring metal nanoparticles onto the surface, without affecting the bulk structure and morphology of nanocarbon supports. In this manner, carboxylic and phenolic groups, with control of their ratio, were formed by air or O_2 MW plasma on CNFs [50] and CNTs [51] to attach Pd and Ru nanoparticles, respectively. Very recently, oxygen-plasma-functionalized CNTs have been presented as supports for Pt–Ru catalysts applied in direct methanol fuel cells for electrochemical methanol oxidation. It has been shown that O_2 plasma treatment leads to the formation of carbonyl (–CO) and carboxylic (–COO) groups on the CNT surface. Pt–Ru nanoparticles dispersed for an optimum plasma treatment time exhibit high catalytic activity toward oxidation of methanol [52]. Iron(II) phthalocyanine, used as an electrocatalyst for the oxygen reduction reaction (ORR) in fuel cells, was also deposited on carbon nanoparticles (Vulcan XC-72) with the aid of plasma pretreatment of the support (N_2, Ar, Ar+O_2, and NH_3 RF plasmas were tested). In some cases, a fivefold increase in the electrocatalytic activity was observed [53].

Considering the issue of carbon nanotubes, we should also mention the use of cold plasma in the preparation of catalysts for the synthesis of CNTs. Gao et al. [54, 55] employed N_2 microwave plasma for this purpose. A very thin Fe film was deposited on a Si substrate by the pulse laser technique and then it was broken by plasma treatment. The nano-sized Fe islands having the density of 1.9×10^{15} m^{-2} and diameters of about 15 nm were obtained. CNTs synthesized on this catalyst were well-aligned, vertically arranged, and had almost the same diameters and density as the nano-islands. Similarly, the nickel catalyst was obtained by converting a Ni thin film into nanoparticles by treatment with microwave H_2 or H_2/N_2 plasmas [56, 57]. Recently, the direct current (DC) plasma as a source of effective ion bombardment, which is crucial for the creation of nano-islands, has been used in the CNT synthesis. It has

turned out that gold nanoparticles produced in this way from a 0.5 nm thick Au film act as efficient catalysts promoting the growth of single-walled CNTs [58]. A small addition of C_2H_2 to H_2 during the DC plasma treatment of Fe thin films causes the simultaneous formation of Fe nanoparticles and coating them with a very thin carbon layer, which reduces sintering of the nanoparticles during the growth of CNTs. This results in a very dense CNT forest, reaching 2.2–2.4 × 10^{16} m^{-2} [59].

2.2. Plasma modification of as-prepared "conventional" catalysts

Many catalysts that are produced for practical use or are already used commercially still need further improvement of their efficiency and selectivity. There have been a lot of research works on the subject and it appears that also in this case, good results can be achieved by plasma treatment. For example, Ar plasma treatment (a corona discharge) of the Ni catalyst used in partial oxidation of methane to syngas causes an increase in the catalytic activity and Ni dispersion. Moreover, the plasma treatment improves the catalytic stability by preventing the deposition of carbon on the Ni catalyst [60]. Similar changes in catalytic properties have been observed for Ni and Pt catalysts treated with He plasma in the dielectric-barrier discharge (DBD) under atmospheric pressure [61]. The DBD technique was also used in order to improve the activity of MnOx catalysts in the catalytic oxidation of nitrogen oxide (NO). The effect of plasma treatment is shown in Figure 5, where increased conversion of NO to NO_2 by O_2 at low temperature (323–523 K) is recorded [62, 63].

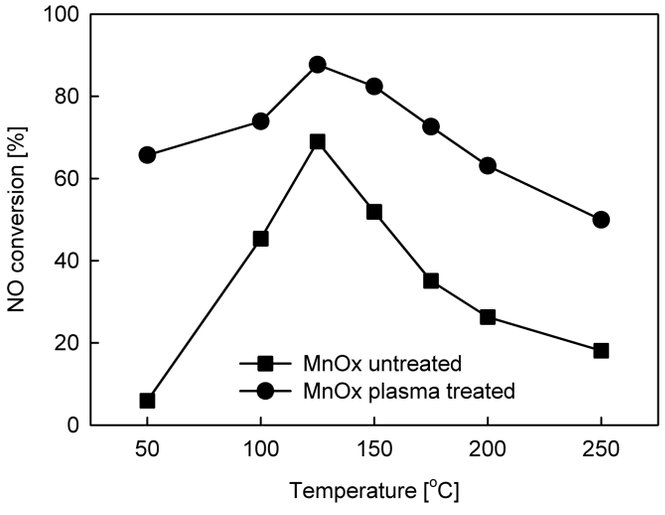


Figure 5. Oxidation activity of MnO_X with and without plasma treatment [63].

An evident improvement in the catalytic properties after the plasma modification of the as-prepared catalysts has recently been reported more and more often. Such catalysts as Pd/TiO_2 for the selective hydrogenation of acetylene [64, 65], Fe–Cu on active carbon for the hydrolysis of carbon disulfide [66], CuO nanowires for oxidation of carbon monoxide [67], or CuO/TiO_2 employed in the reduction of nitrogen oxides [68] have shown higher efficiencies,

only when the plasma treatment process was added after the catalyst preparation. Of course, in any case, it is necessary to choose an appropriate type of plasma and select optimized parameters of the treatment process. An example is given in Figure 6, where one can observe the effect of plasma exposure time (Ar MW plasma) on the conversion and selectivity for the above-mentioned CuO/TiO_2 catalyst tested in the reaction [68]:

$$NO + CO \rightarrow \frac{1}{2} N_2 + CO_2 \quad (4)$$

This result indicates that a remarkable increase in activity and selectivity is achieved depending on the plasma treatment time. However, this clear improvement is attributed not only to a greater dispersion of the catalyst but also to changes in its chemical structure. It has been suggested that highly active oxygen species (O*) are formed on the surface during plasma treatment, which leads to positive changes in the reaction path.

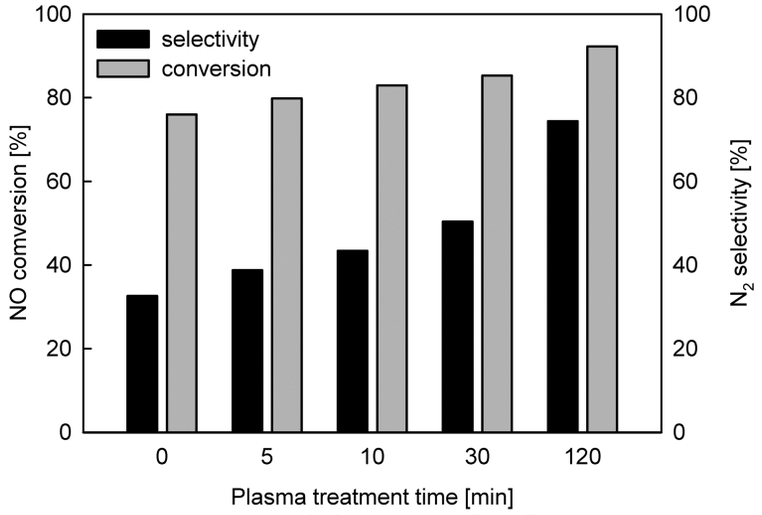


Figure 6. Catalytic performances for reaction (4) over CuO/TiO_2 catalysts following different microwave plasma treatment times [68].

The plasma treatment has also turned out to be very useful for the regeneration of spent catalysts. It has been found that the rate of reduction is several times higher for the plasma-treated deactivated catalysts than for the untreated ones. Furthermore, activity of the regenerated catalyst is usually higher than that of the fresh catalyst [1]. Application of the plasma method is especially important in the case of nanocatalysts, whose catalytic activity depends strongly on their size, so only low-temperature regeneration methods are acceptable. The plasma regeneration (O_2 DBD plasma) of TiO_2-supported gold nanoparticle catalysts (Au/TiO_2) has been successfully used to a great enhancement of catalytic activity for CO oxidation over the completely deactivated Au/TiO_2 [69]. Recently, a more sophisticated plasma treatment has been used to regenerate tungsten carbide (WC), which is considered a promising replace-

ment for precious metal-based electrocatalysts for fuel cells. Mild treatment of WC foil with atomic oxygen generated in a plasma source operating in the atom mode (with an ion trap) allows a controlled removal of graphitic carbon from the WC surfaces without causing oxidation of WC [70].

3. Plasma sputtering of catalytic nanoparticles

Ultrafine particles are a particularly interesting form of catalysts due to their large specific surface and less-perfect crystal lattice with a large number of vacancies, which induces high catalytic activity. One of the most efficient methods of producing such particles of sizes from several to tens of nanometers is the cold plasma sputtering [71]. In this technique, positive ions that are produced in plasma generated in an inert gas, for example Ar, bombard the target surface and cause sputtering of its material. The sputtered material condenses on the substrate that is located outside of the plasma region. If some reactive gases are used (e.g., O_2, N_2, CH_4), the target material takes part in chemical processes during sputtering and finally a new converted material is deposited. This is the so-called reactive plasma sputtering. Simultaneously, two or more different targets can be specified, and the process can also be enhanced by magnetic field (magnetron plasma sputtering). So, as one can see, the plasma sputtering has great technological potential for the production of nanocatalysts. By choosing the appropriate process parameters, the structure, size, and quantity of nanoparticles can be controlled. As an example, the dependence of diameter of Pd nanoparticles on the sputtering time (Ar plasma, 100 MHz) is shown in Figure 7.

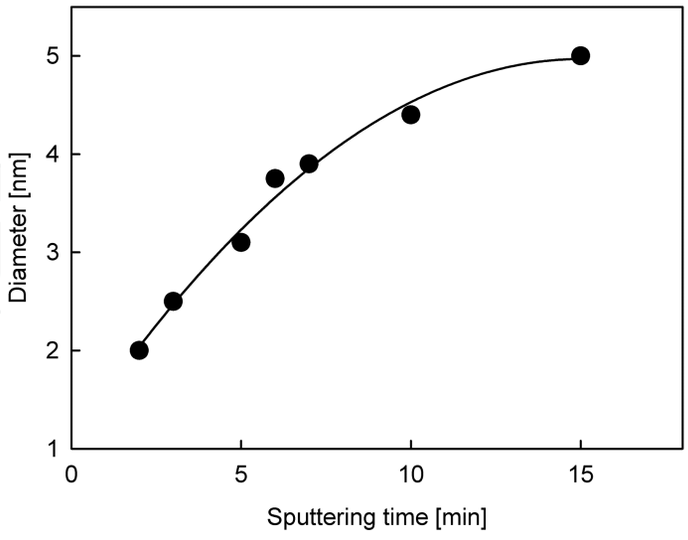


Figure 7. Pd nanoparticles diameter on the time of plasma sputtering (on the basis of Ref. [72]).

The metal and metal oxide nanoparticles are used primarily as catalytic materials for fuel cell electrodes, and mainly in this respect, the plasma sputtering has been intensively investigated

over the past 15 years [17]. It has been shown that Pt, Pd, Rh, Pt_XRh_Y, Pt_XRu_Y, Pt-RuO_X, Ni_XZr_Y, PtNiZr, NiZrPtRu, CoO_X, NbO_X, NbO_XN_Y, Pd_XAu_Y, and others can be plasma-sputtered and deposited in the electrocatalytic active form [73–85]. In many cases, they exhibit higher activity than conventionally prepared electrodes, but the possibility to significantly reduce the amount of catalytic material used is the most important. It has been shown that the catalytic electrodes could be prepared with a platinum loading down to 0.005 mgPt/cm^2, which is drastically lower than that for conventional Pt electrodes (0.5–1.0 mgPt/cm^2), with no detrimental effect on the fuel cell performance. Figure 8 presents the specific power on the current density for a PEM fuel cell with a Pt-sputtered anode, for various loadings of the catalyst. The advantageous effect of reducing the amount of catalyst is clearly visible [86].

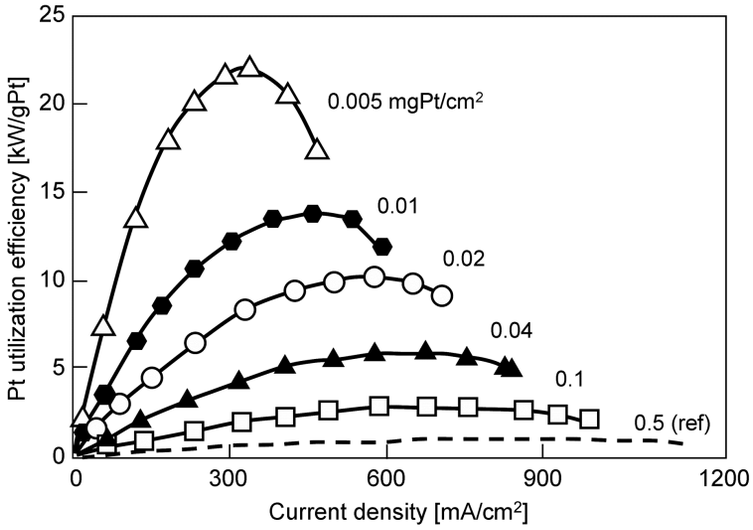


Figure 8. Platinum utilization efficiency versus current density for plasma-prepared cathodes with different Pt loading (mgPt/cm^2). For comparison, the results for "classic" Pt cathode with Pt loading of 0.5 mgPt/cm^2 are presented [86].

The method of plasma spraying has proven to be very useful in the preparation of 3D-catalysts [17]. Already in the early 2000s, Brault et al. [87, 88] applied this method to introduce Pt clusters into a porous carbon material forming 3D-electrodes for PEM fuel cells. They obtained Pt nanoclusters of 3.5 nm, which penetrated the porous carbon electrode up to 2 μm deep. It should also be emphasized that although the electrode work was comparable to commercially available electrodes, it had the platinum density 4.5 times lower and hence was significantly more effective. Recently, a new pathway in the design of 3D-electrodes has been proposed, namely a combination of the methods of plasma polymerization (PECVD) and plasma sputtering. This dual-plasma process, i.e., the synthesis of catalytic thin films made of Pt nanoclusters (3–7 nm) embedded in a porous hydrocarbon matrix, was carried out by simultaneous plasma-polymerization of ethylene and sputtering of a platinum target. The metal content in the films could be controlled over a wide range of atomic percentages (5– 80%) [89]. Great possibilities of this method have encouraged attempts to produce non-noble metal catalysts for PEM fuel cells. Metals such as copper, cobalt, and iron have been sputtered and embedded into the matrix formed via the PECVD of pyrrole [90–93]. Plasma polymerized

pyrrole (pp-pyrrole) exhibits high electrical conductivity and gas permeability as well as good chemical stability, so that together with the sputtered metal clusters forms an excellent nanocomposite, which can act as a 3D-catalyst.

4. Plasma-deposited (PECVD) thin films with catalytic properties

One of the most promising methods of producing new catalytic structures is the plasma deposition of thin films from organic and metalorganic precursors most frequently supplied to the plasma reactor in the gas phase. This method of thin-film deposition, well known as the plasma polymerization or plasma-enhanced chemical vapor deposition (PECVD), has already been used to fabricate a lot of thin-film materials for various practical applications [94]. In the late 1980s, a possibility of using PECVD to produce thin films having potential catalytic properties, such as Pd, Rh, Pt, was already mentioned [95–98]; however, only recently the involvement of this method in the field of catalysis has become a reality [3, 15, 17].

4.1. Background

Metalorganic compounds (their molecules are composed of a metal atom surrounded by organic or organic-like (e.g., CO) ligands) are key precursors for the PECVD of thin films displaying catalytic properties, in which the catalytic activity is related to the presence of metal or metal oxide clusters in amorphous or nanocrystalline forms. However, thin films possessing potential catalytic properties plasma-polymerized (pp-) from typical organic (without metal) precursors, wherein organic functional groups act as active centers, have also attracted attention. It was found quite a long time ago that the films containing organic moieties of specific electronic structure, for instance, the quinone-type groups formed in pp-4-vinylpyridene [99] or the protonated amine groups created in pp-allylamine [100], exhibit electrocatalytic activity. Recently, this idea has returned – thin films have been deposited onto silica–alumina powders by plasma polymerization of 1,2-diaminocyclohexane to prepare amine-immobilized solid base catalysts. The existence of amine moieties has been confirmed by solid-state ^{13}C NMR, FTIR, and XPS analyses. The silica–alumina powders with these films have shown strong base catalytic activity, e.g., in Knoevenagel condensation reaction between benzaldehyde and ethyl cyanoacetate [101].

As already mentioned, the metalorganic precursors are introduced into plasma reactors mainly in the gaseous form. Sometimes, however, this poses a problem because of the low vapor pressure of such compounds. To get around this difficulty, an innovative method of production of catalytic films by the PECVD has been proposed lately. In this method, compounds are injected into a plasma reactor by means of, for example, an atomizer, in the form of aerosols created from liquid solutions of precursors. Cobalt oxide thin films for catalytic applications were deposited this way using the aerosol from a solution of cobalt carbonyl ($Co_2(CO)_8$) and hexane [102, 103]. Likewise, a series of hybrid silica-based catalysts containing various metals (Ti, V, Zr, Sn, Mn, Fe, Co) were produced utilizing nano-sized droplets (15–50 nm) sprayed from a solution of a selected metalorganic precursor, tetraethoxysilane ($Si(OC_2H_5)_4$), and an

organic solvent, and then injected into a DBD plasma reactor [104]. Precursors can also be introduced directly to the plasma chamber as a solid phase mixture with a powdered support. During plasma operation, the precursor is transferred into the gas phase and then involved in the deposition processes [105–107].

The plasma deposition (PECVD) of thin films from metalorganic precursors should also include a fairly sophisticated method called the plasma-assisted atomic layer deposition (ALD). This is true nanotechnology, allowing ultra-thin films of a few nanometers to be deposited in a precisely controlled way via subsequent cycles that generate layer-by-layer growth [108]. Very recently, the ALD has emerged as an interesting tool for the atomically precise design and synthesis of catalytic materials with a controlled distribution of size, composition, and active site [109].

Occasionally, an incipient wet impregnation of the support by a solution of metalorganic precursor, followed by plasma treatment (e.g., with O_2 plasma) is applied to preparation of potential catalysts, such as CoO_X on zirconia [110], or CrO_X on silica [111]. However, this procedure is not a typical PECVD process in the gas phase.

Examples of metalorganic precursors used for the plasma deposition of thin films having potential catalytic activity are summarized in Table 1. Apparently, the PECVD method can be successfully used to produce a wide variety of films, comprising both metal and metal oxide catalytically active phases.

Metalorganic precursor	**Denotation**	**References**
platinum(II) acetylacetonate	$Pt(acac)_2$	[107,112,113]
palladium(II) acetylacetonate	$Pd(acac)_2$	[114]
palladium(II) hexafluoroacetylacetonate	$Pd(hfac)_2$	[115,116]
rutenium(II) bis(ethylcyclopentadienyl)	$Ru(EtCp)_2$	[117,118]
cobalt(III) acetylacetonate	$Co(acac)_3$	[119]
cobalt(II) bis(2,2,6,6-tetramethyl-3,5-heptanedione)	$Co(TMHD)_2$ $Co(dpm)_2$	[120]
cobalt(II) bis(cyclopentadienyl)	$CoCp_2$	[121]
cobalt(I) cyclopentadienyldicarbonyl	$CpCo(CO)_2$	[122-124]
dicobalt octacarbonyl	$Co_2(CO)_8$	[102,103]
titanium(IV) tetraisopropoxide	TTIP	[125-131]
titanium(IV) butoxide	TNBT; $Ti(OBu)_4$	[132]
titanium(IV) ethoxide	$Ti(OEt)_4$	[133]
titanium(IV) diisopropoxidebis(2,2,6,6-tetramethyl-3,5-heptanedionate)	$Ti(O\text{-}i\text{-}Pr)_2(thd)_2$	[134]
zirconium(IV) acetylacetonate	$Zr(acac)_4$	[113]

Metalorganic precursor	Denotation	References
zirconium(IV) tetra(*tert*-butoxide)	ZTB	[135]
zirconium-n-propoxide	ZNP	[104]
iron(III) acetylacetonate	$Fe(acac)_3$	[136]
iron(II) bis(hexafluoroacetylacetonate) (N,N,N',N'-teramethylenediamine)	$Fe(hfa)_2TMEDA$	[137]
tert-butylferrocene	TBF	[138]
iron(0) pentacarbonyl	$Fe(CO)_5$	[139,140]
copper(II) acetylacetonate	$Cu(acac)_2$	[124]
chromium(III) acetylacetonate	$Cr(acac)_3$	[105,106]

Table 1. Examples of metalorganic precursors for PECVD of catalytic films.

Generally, there are two possible ways to start the decomposition of metalorganic molecules in the PECVD process. The ligands of the precursor can be decomposed in the gas phase, and the products of the process then participate in the formation of the film on the substrate surface, or the precursor molecules are first adsorbed on the surface without decomposition. Then, their decomposition occurs during the interaction of plasma with the substrate. Investigations of the preparation process of CrO_X deposited from chromium(III) acetyloacetonate ($Cr(acac)_3$) in microwave plasma on a Zr-based support have evidently shown that during the PECVD process adsorption of the precursor molecules on the support probably takes place by cleavage of one ligand. Further plasma operation causes the gradual destruction of ligands and formation of a CrO_X structure. This chemical process is schematically presented in Figure 9 [106]. On the other hand, the study on plasma-polymerized ZrO_2 films from zirconium(IV) tetra-tert-butoxide in a mixture with oxygen has shown that the gas-phase reactions have a direct impact on the deposition process. Mass spectra of the plasma have revealed a number of species, including CH_3^+, $C_2H_4^+$, CHO^+, $C_2H_5^+$, CH_3CO^+, $C_4H_6O^+$, Zr^+, ZrO^+, ZrO_2H^+, $ZrO_3H_3^+$, $ZrO_4H_5^+$, $ZrO_3C_3H_7^+$, which initiate processes of the film formation [135].

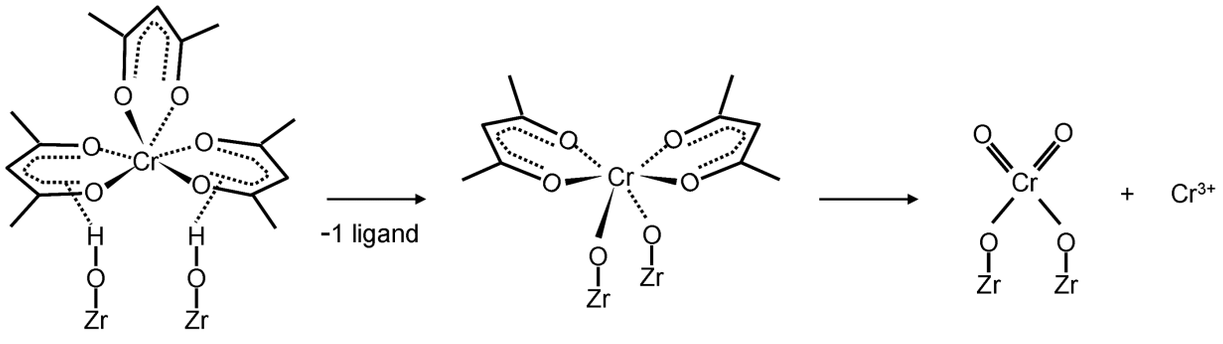


Figure 9. Schematic representation of possibly adsorption of $Cr(acac)_3$ on Zr-based support and stepwise plasma destruction of the precursor molecule, which leads to CrO_X with Cr^{3+} and Cr^{6+} species [106].

By carefully controlling the process parameters, the ligands can be completely removed, leaving only "pure" metal or its oxides. Very often, however, some amount of carbon is present in deposits. To eliminate the carbon contamination, treatment with oxygen plasma, heated substrates during the deposition, and heat treatment after the deposition have been practiced [3, 15].

An appropriate choice of the PECVD process conditions also permits control of the film structure. Amorphous films such as TiO_2 films of 7–120 nm thickness (deposited from titanium(IV) butoxide) can be obtained and after thermal treatment at 713 K transformed into nanocrystalline anatase films having a grain size of about 15 nm [132]. Similar results concerning the conversion of TiO_2 from amorphous in crystalline phase of anatase structure as a result of thermal treatment were shown by Cho et al. [129] for films deposited from titanium tetraisopropoxide. However, nanocrystalline structure can also be produced directly in the PECVD process, as is the case with TiO_2 films deposited on the heated substrate, where the crystalline domains of 40–90 nm have been obtained [130]. The structure of the films can be controlled by the type of support as well. When TiO_2 films were produced form $Ti(O\text{-}i\text{-}Pr)_2(thd)_2$, the use of quartz substrates resulted in the formation of films showing predominantly the anatase crystallographic structure. On the other hand, only the rutile phase was found in the case of silicon wafers and nearly amorphous phase for metallic Ni [134].

Finally, the molecular structure of deposited films can be controlled using mixtures of metalorganic precursors. For example, interesting films of CoO_X doped with Cu were prepared by the PECVD from a gas mixture of $CpCo(CO)_2$ and $Cu(acac)_2$. It was found that pure cobalt oxide films were mainly composed of Co_3O_4 in the form of nanoclusters, whereas the Cu doped films were much more complex: CoO_X (also Co_3O_4), mixed Co–Cu oxides, and CuO_X nanoclusters were detected. Preliminary catalytic tests showed that the films of CoO_X doped with Cu initiated the catalytic combustion of n-hexane at a lower temperature, compared with the pure cobalt oxide films [124].

Among the biggest advantages of films produced by the PECVD method, beyond their structural diversity that cannot be achieved by any other method, is their very thin form (in the order of nm). This is of particular importance, on the one hand, to save materials, and on the other hand, such thin films are ideal for new constructions of catalytic structured reactors and electrodes for fuel cells. Currently, the most extensively studied plasma-deposited materials with possible applications as catalysts include some noble metal-based films (e.g., Pt, Pd, Ru) and non-noble transition metal-based films, which exist mainly in the form of oxides (e.g., TiO_2, CoO_X, FeO_X).

4.2. Noble metal–based films

Platinum-based materials (Pt or Pt alloys) are the best catalysts for many reactions, especially for hydrogen and methanol oxidation as well as oxygen reduction, which are at the core of fuel cell technologies. Unfortunately, Pt is a precious and very expensive metal. Besides, the stability of Pt and Pt alloys becomes a serious problem. Hence, extensive research has been underway to overcome these difficulties and new methods to ensure consumption of smaller

amounts of platinum and at the same time provide more stable and effective catalysts are being sought.

In addition to plasma sputtering, which is a very promising technique (see: Sec. 3), the plasma polymerization method (PECVD) has also been tested as a tool for the preparation of platinum thin-film catalysts. A platinum metalorganic complex, ($Pt(acac)_2$), was used by Dhar et al. [112] as a precursor for the PECVD carried out in an RF discharge. The plasma-polymerized film was then calcined to drive off organic material, leaving behind a catalyst-loaded substrate. The same procedure was used to prepare a composite consisting of a ZrO_2 support and Pt catalyst. The support and catalyst were deposited on a metallic substrate by the PECVD as alternate layers from $Zr(acac)_4$ and $Pt(acac)_2$, respectively. It was found that Pt agglomerates were embedded in the zirconia support [113]. Recently, the mechanism of formation of Pt nanoparticles on carbon black powder used as a support, during plasma deposition from $Pt(acac)_2$ has been more closely investigated. It has been proposed that some oxygenated surface groups or structural defects are formed at the surface of carbon under the influence of plasma. These surface defects act as anchoring sites for the nucleation of Pt nanoparticles. Thus, by controlling the processes of precursor decomposition and formation of surface defects, through an appropriate choice of plasma parameters, the size and concentration of nanoparticles can be controlled [107].

Another important noble metal, which has been widely used as a catalyst in various syntheses, is palladium. In case of palladium, some attention has been paid to the plasma assisted ALD method. Pd thin films were deposited on substrates at low temperatures (≤ 373 K) by means of a remote inductively coupled hydrogen plasma and frequent use of $Pd(hfac)_2$ as a precursor. This way, Ten Eyck et al. [115] obtained films of the thickness from 1.66 to 3.87 nm after 150 cycles of pulsed ALD, depending on the type of substrate. An additional O_2 plasma step in each cycle yielded virtually 100% pure palladium thin films composed of nanometric crystalline grains, the size of which could be controlled by the number of deposition cycles [116]. Investigations performed on Pd films prepared by the typical PECVD process (from $Pd(acac)_2$) showed that the as-deposited films were amorphous and only after thermal treatment at 623 K, Pd nanocrystalline clusters of 5–10 nm size were formed [114].

The group of important noble metals used in catalysis includes ruthenium as well. As in the case of Pd plasma-deposited films, particular attention has been paid to the plasma-assisted ALD method. By using a $Ru(EtCp)_2$ precursor and $N_2/H_2/Ar$ or NH_3/Ar plasmas as reactants for the appropriate steps in the deposition cycles, very thin films of ruthenium (with the growth rate of about 0.17 nm/cycle on SiO_2 substrates), containing very low amounts of oxygen and carbon, were produced [117,118]. The same precursor ($Ru(EtCp)_2$) was used in our laboratory to perform typical PECVD process for preparing ruthenium films. XPS analyses indicated that the as-deposited films contained only metallic ruthenium (Ru^0); however, after calcination at 773 K in air, a fraction of RuO_2 (Ru^{4+}) appeared. Spectra of Ru 3d5/2 obtained for the as-deposited and calcined films are shown in Figure 10. The films were tested in the catalytic reactions, such as methanation of CO_2 [141] and water splitting [142].

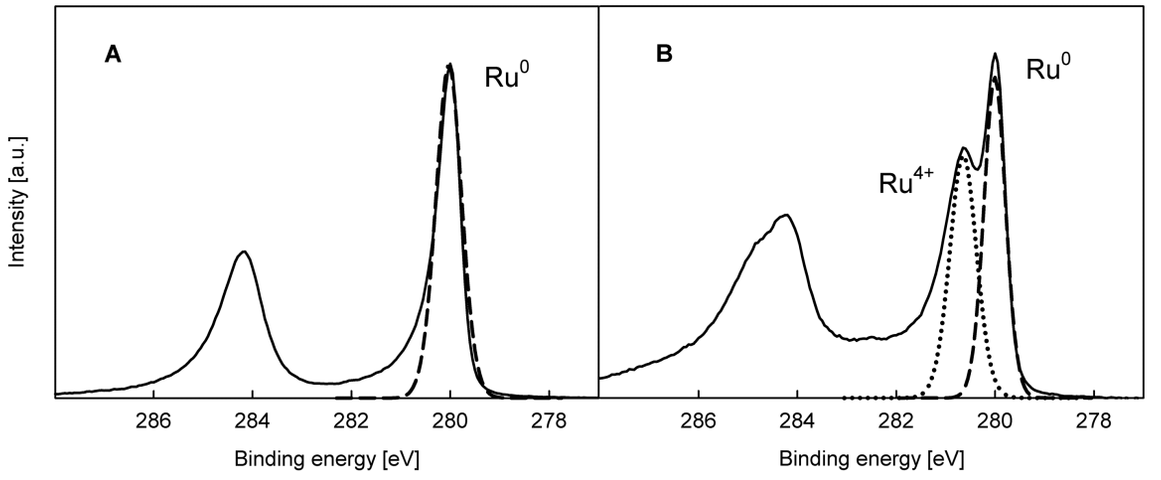


Figure 10. XPS spectra of Ru 3d5/2 for as-deposited (A) and calcined (B) films obtained by PECVD from $Ru(EtCp)_2$.

4.3. Non-noble transition metal–based films

Transition metals, mainly in the form of oxides, are well known as catalysts in many chemical and photochemical reactions. Among these oxides, for a long time TiO_2 has belonged to the most intensively studied compounds, mainly because of its unique photocatalytic activity [143]. The plasma deposition of TiO_2 thin films is prominent among the methods of producing this material and many results have already been published on this subject; some of them were mentioned above [129, 130, 132, 134], others can be found in the reviews (for example, see [15, 144]). In most reported works, either $TiCl_4$ or Ti alkoxides (mainly titanium tetraisopropoxide) are used as precursors of the PECVD process, resulting in amorphous or crystalline films having the nonstoichiometric (TiO_X) or stoichiometric (TiO_2) structure. Physicochemical and catalytic properties of all of these films are strongly dependent on their structure, which can be effectively controlled by the deposition conditions [125–128, 131, 133].

Other metal oxides important from the standpoint of catalysis are cobalt oxides (CoO_X) and iron oxides (FeO_X). Their thin films produced through the PECVD have recently been of particular interest.

4.3.1. CoO_X-based films

The first attempts to produce films from cobalt metalorganic precursors by the PECVD method were undertaken in the early 1980s [145,146], but they have been more closely studied only recently [102, 103, 119–122, 124, 136]. This is related to wide possibilities of application of CoOx films in new structural reactors for catalytic synthesis as well as in electro- and photo-catalyses carried out in fuel cells and water splitting processes. Various precursors have been used (see, Table 1), but one of the most convenient is $CpCo(CO)_2$, because it is liquid at room temperature and highly stable, which facilitates control of the plasma process.

The nanostructure of plasma-deposited CoO_X films, which is crucial for catalytic properties, can be controlled by the type of precursor, plasma process conditions, and nature of supports.

For example, small particles of CoO_x 2–10 nm in diameter were found in the plasma-deposited films on TiO_2 supports [119]. When CoO_x films were produced on a glass substrate at elevated temperatures (423–673 K), columnar grains of the average diameter between 35 and 60 nm were formed on the film surface [147]. Highly pure and strongly oriented Co_3O_4 thin films, with features dependent on the used substrate and adopted growth temperature, were obtained by the PECVD on single crystals, such as MgO(100) and $MgAl_2O_4$(100) [120]. In turn, the plasma deposition from liquid solutions of Co compounds sprayed into the plasma reactor gave thin films containing nanocrystals 15 or 40 nm in size, depending on the type of precursor and the PECVD process conditions [102]. If such films are post-treated with Ar and O_2 plasma, the crystal nano-catkins, which can increase the contact area of the catalyst, are formed containing particles of Co_3O_4 3–12 nm in size [103].

The research conducted in our laboratory on CoO_X films produced by the PECVD from $CpCo(CO)_2$ has confirmed that the structure of these films can be controlled by the conditions of the deposition [3, 122, 123]. As deposited, thin films (25–750 nm) composed of a hydrocarbon matrix and amorphous CoO_X were obtained. However, only moderate thermal treatment was enough to transform the amorphous films into films possessing the nanocrystalline structure of cobalt spinel (Co_3O_4). The formation of such nanocrystals was confirmed not only by electron diffraction analysis but also by Raman spectroscopy measurements, an example of which is shown in Figure 11.

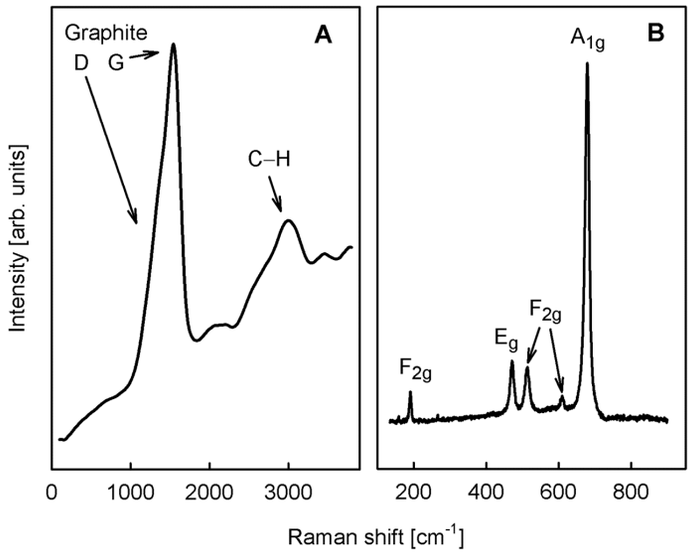


Figure 11. Raman spectra for: (A) thin film of hydrocarbon matrix with amorphous CoO_X, (B) thin film of nanocrystalline Co_3O_4 [123].

It has also been found that the size of nanocrystallites is controllable by the thermal treatment. To investigate this effect precisely, an energetic laser beam was used as the heat source. The dependence of the crystallite size on the time of laser treatment is illustrated in Figure 12. As can be seen, the average size of the Co_3O_4 nanocrystallites increases with the treatment time reaching a constant value. On the other hand, the concentration of nanocrystallites is almost

constant throughout the treatment. The maximum size and concentration of the nanocrystallites can in turn be controlled by the parameters of the plasma process. It has already been shown [123] that with an increase in the precursor flow rate, the maximum size of nanocrystallites, after the thermal treatment, increases.

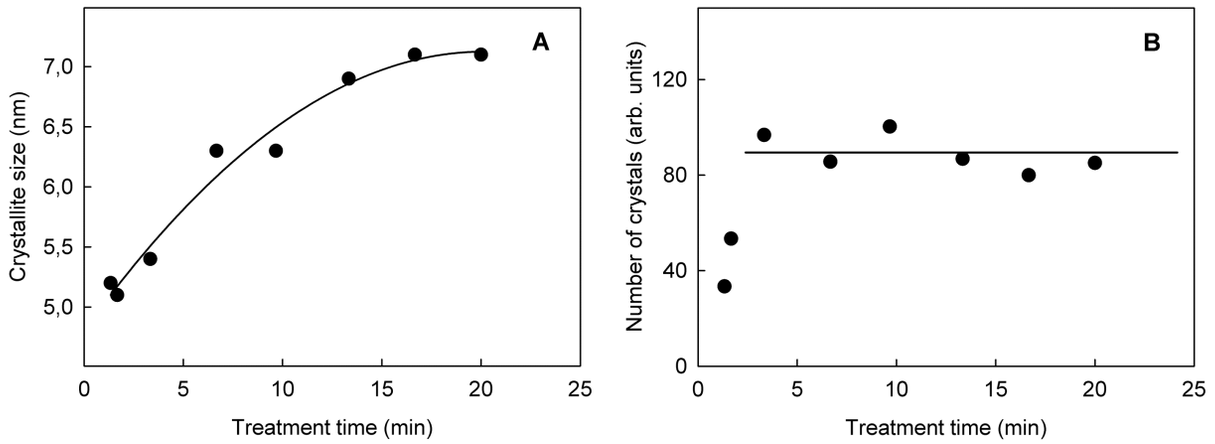


Figure 12. The size (A) and concentration (B) of Co_3O_4 nanocrystallites in a film plasma deposited from $CpCo(CO)_2$, in dependence on the laser treatment time.

The above results represent a further step toward the molecular engineering of catalysts, where the desired nanostructure of material and thus its catalytic activity can be designed.

4.3.2. FeO_X -based films

The recent interest in the plasma-deposited FeO_X thin films has been prompted primarily by the possibility of using these films as photocatalysts in the water splitting process [137, 139, 140, 148, 149]. Various types of FeO_X films can be prepared, depending on the precursor used (see, Table 1) and deposition process conditions. Already twenty years ago, Fujii et al. [136] showed that using the same precursor and constant RF plasma power, a wide range of FeO_X structures was obtained by controlling the O_2 flow rate and substrate temperature (T_S) during the deposition process. These results are summarized in Figure 13. As can be seen, at low values of the O_2 flow rate, amorphous films are formed independent of T_S. When the flow rate increases, thin films of spinel-type iron oxide (Fe_3O_4), which are composed of both Fe^{2+} and Fe^{3+}, are created. Usually, however, it is not a pure fraction, but rather Fe_3O_4–γ-F_2O_3 intermediate phase. At the O_2 flow rate higher than 30 cm^3/min, thin films composed of Fe^{3+} are formed, namely α-Fe_2O_3 (at T_S = 600–750 K) and β-Fe_2O_3 (at T_S = 450–650 K), although the films of single phase β-Fe_2O_3 cannot be obtained and this structure occurs only in coexistence with the spinel-type iron oxide. However, by appropriate selection of the PECVD conditions, it is possible to obtain films containing pure β-Fe_2O_3. Such films with columnar arrays of β-Fe_2O_3, characterized by a preferred (100) growth direction and highly porous structure, have been successfully plasma deposited from a fluorinated precursor ($Fe(hfa)_2TMEDA$) in a mixture with Ar and O_2 [137].

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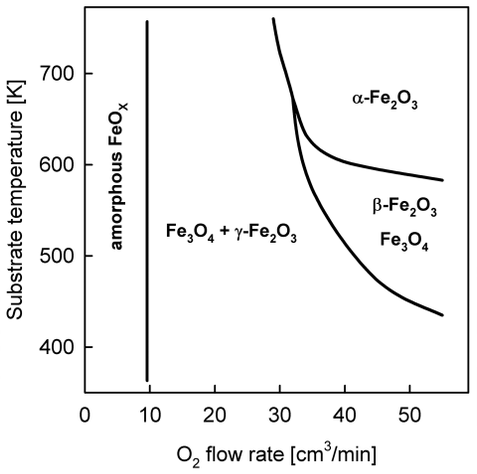


Figure 13. Formation diagram of iron oxide films deposited from $Fe(acac)_3$ at a constant RF plasma power (400 W) (on the basis of Ref. [136]).

The structure of deposited iron oxide films can also be modified by post-treatment. In Figure 14, examples of the XPS spectra of Fe 3p, concerning films deposited from $Fe(CO)_5$ in our laboratory, are shown. A clear change in the structure as a result of thermal treatment (723 K, in air) is observed. The as-deposited film contains Fe^{2+} and Fe^{3+}, which in combination with the results of X-ray diffraction and Raman spectroscopy indicates a spinel-like structure. After thermal treatment, only the completely oxidized form Fe^{3+} is present on the film surface. It has been found that in these films Fe^{3+} is associated with γ-Fe_2O_3 nanoparticles [150], which are already known as an effective catalyst [151]. An opposite process, i.e. the change of the film structure containing only Fe^{3+} to that containing a mixture of Fe^{3+} and Fe^{2+}, can be carried out using hydrogen plasma treatment. This way, hematite (α-Fe_2O_3) films were transformed to Fe_3O_4:α-Fe_2O_3, with precise control of the Fe^{3+} to Fe^{2+} ratio. This treatment substantially improved optical absorption, enhanced electrical conductivity, and improved transport properties due to a valence dynamic in the film among different iron oxidation states [140].

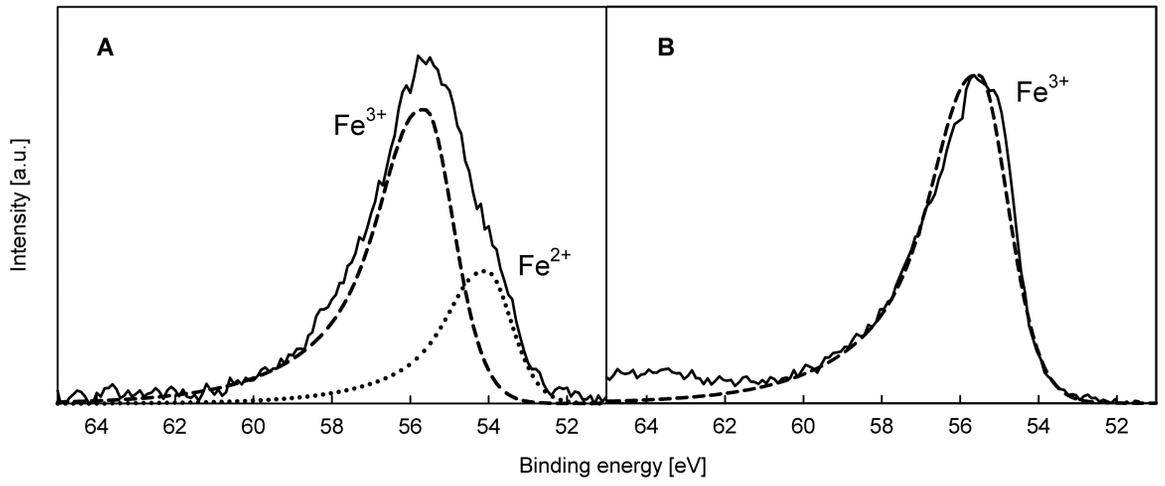


Figure 14. XPS spectra of Fe 3p for as-deposited (A) and calcined (B) films obtained by PECVD from $Fe(CO)_5$.

A wide range of possibilities provided by the PECVD method allows us to design and produce more sophisticated structures at the molecular level. It is also true for iron oxide films, where, for example, Barreca et al. [137] replaced a part of oxygen atoms with fluorine atoms in the film structure. They showed that a noticeable switch from *n*- to *p*-type conductivity occurred upon increasing the fluorine amount in the films. This transformation in the electronic structure resulted in the extended charge carrier lifetime, making F-doped β-Fe_2O_3 films an efficient water oxidation catalyst. Recently, more complex nanosystems based on iron oxide films have also been prepared. Such nanosystems, for instance, including Fe_2O_3–CuO [148] and Fe_2O_3–Co_3O_4 [149], are synthesized by using a two-step plasma-assisted strategy. First, the iron oxide nanostructured thin film (as a host) is deposited by the PECVD and then CuO or Co_3O_4 nanoparticles (as guests) are over-deposited on the host matrix by means of plasma sputtering of Cu or Co and annealing in the air. The obtained structures based on the combination of *p*-type (CuO and Co_3O_4) and *n*-type (Fe_2O_3) semiconducting oxides, which create the *p*-*n* junctions responsible for the improved separation of electron–hole pairs, are highly promising as catalysts for the photochemical splitting of water.

In addition, the advanced structures based on plasma-deposited iron oxides include Fe_2O_3 thin films that very recently have been produced by plasma-enhanced atomic layer deposition (ALD) from tertiary butyl ferrocene and O_2 plasma. The films deposited below 523 K are amorphous but can be converted into hematite (α-Fe_2O_3) with (104) preferential orientation and average crystallite size of 35 nm by annealing in He [138].

4.4. Potential applications of the plasma-deposited (PECVD) catalytic films

The three main features of the PECVD method are the source of its attractiveness and broad prospects in the production of new catalytic species, namely – the ability of preparing very thin (<< 1 μm) films, the possibility of precise control over molecular structure and nanostructure of the films by selecting appropriate precursors and conditions of the manufacturing process, and finally, the possibility of obtaining 3D structures through the use of copolymerization of two or more precursors in the PECVD process or combining the PECVD and plasma sputtering processes together.

Current research on the potential possibilities of the application of catalysts produced by the PECVD is focused on the structured reactors, where the deposition of very thin catalytic coatings is the key problem, and on the PEM fuel cells and photoelectrochemical cells for water splitting, which need cheap and efficient electro- and photocatalysts.

4.4.1. Structured reactors

Development of the new and improvement of the existing heterogeneous catalytic processes are actually tasks of great practical importance in such areas as chemical and petrochemical industries, as well as in environment protection, particularly in catalytic combustion of volatile organic compounds (VOCs) and CO_2 conversion into value-added products. Conventionally used reactors for catalytic combustion and CO_2 conversion are packed bed (filled with a bed of catalytic grains) and monolithic reactors. The first type can be regarded as a slightly old-

fashioned solution showing high flow resistance and low effectiveness of the catalyst grains, which in turn leads to high spending on catalyst material. Monolithic reactors are currently the standard equipment used for catalytic combustion since they provide better performance compared with packed bed reactors. However, monolithic reactors often fail in this process. This is because the so-called fully developed laminar flow occurs throughout most of the monolithic channels. Therefore, mass transfer at the developed laminar flow is rather low and weakly affected by the fluid velocity. Taking into account the high dilution of VOCs in large gas streams, the process is mainly controlled by the mass transfer, which imposes the use of long reactors to secure high conversion of VOCs. This in turn gives rise to an undesired high pressure drop and poor catalyst exploitation. An ideal reactor for combustion of VOCs should thus allow both high mass transfer coefficients and reasonably low flow resistance. The same requirements apply to many other heterogeneous catalytic reactions [16,152].

One of the possible paths for progress in this area is the development and application of new geometrical forms of catalysts. Structural reactors equipped with metallic fillers made of wire gauzes displaying highly enhanced transport properties proved to be an interesting option for all types of catalytic processes. Although such a solution based on noble metal catalysts has been known for a long time, for example, reactors filled with stacked platinum woven wire gauzes used for ammonia oxidation, the extension of this concept to other non-noble metal-based catalysts faces serious problems. The crucial difficulty is the deposition of appropriate thin, uniform, well-adhered, and catalytically effective films on wire supports that form fine microstructural meshes, such as the one shown in Figure 15. The most important is the deposition process should not change the elaborate geometry of the meshes.

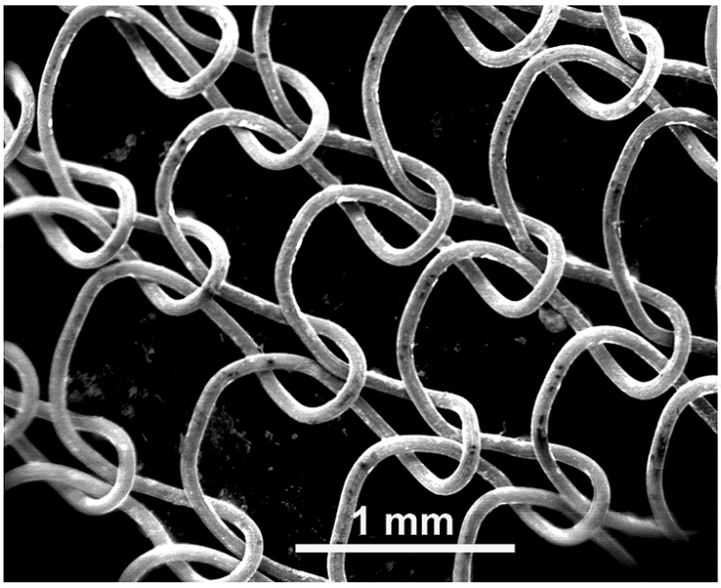


Figure 15. SEM image of a wire gauze made of kanthal with thin CoO_X film, used in our experiments with structured reactors.

The PECVD is one of the most promising methods of producing thin catalytic films on metal gauzes. Research on this subject was started in our laboratory in 2007. Catalytic combustion

of *n*-hexane, as a representative of VOCs, and CoO_X as well as CoO_X–CuO_X based thin films produced by the PECVD, as catalysts of the combustion process, have been intensively investigated providing excellent results [122, 153–156]. It has been found that the plasma-deposited cobalt oxide catalyst showing a dispersed spinel (Co_3O_4) structure (see: Sec. 4.3.1) proves active in the *n*-hexane combustion as compared with commercial Pt catalysts. Even better results have been obtained for Cu-doped CoO_X films that have the lowest reaction initiation temperature (493 K). It has also been concluded that the gauze carrier enhances the mass transport in the reactors preventing the diffusional limitation of the reaction rate. Compared with the standard monolithic converter, it allows a reduction in the reactor length by around 50 times with a 20% increase in the pressure drop. These results encouraged undertaking the research on a larger scale with a prospect of possible future industrial applications. Experiments with *n*-hexane combustion on the plasma-deposited Co_3O_4 catalysts were successfully carried out in a large structured reactor (gas stream up to 10 m^3/h STP) [16].

More recently, the research on CO_2 methanation process using thin films of catalysts plasma deposited on wire gauze carriers has been initiated by our team. The CoO_X (see: Sec. 4.3.1) and Ru-based (see: Sec. 4.2) films have been tested. Sample results are shown in Figure 16. Although these are only preliminary results, they confirm the catalytic activity of the films in the process of CO_2 methanation and encourage further research in this area.

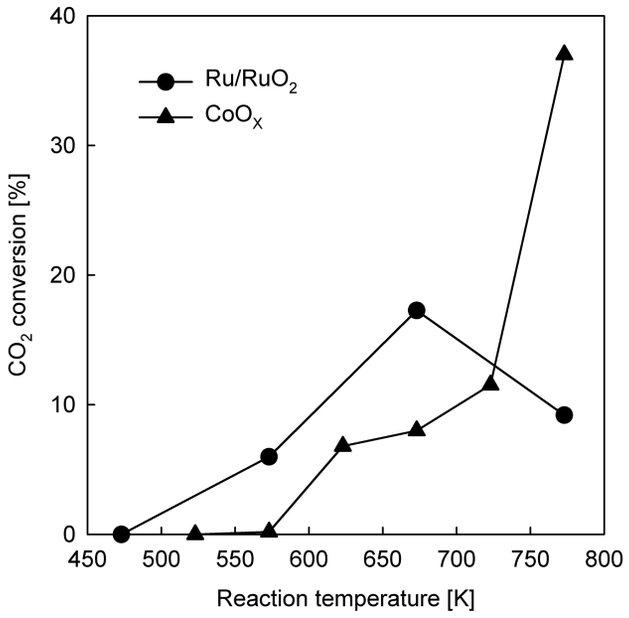


Figure 16. Conversion of CO_2 to CH_4 as a function of the process temperature for two different plasma-deposited catalytic films [141].

4.4.2. Fuel cells

Current studies on thin films produced by the PECVD, which can be used as catalytic systems in proton exchange membrane fuel cells (PEMFC), are primarily focused on finding new

solutions that could compete with platinum electrodes – would be cheaper and exhibit at least comparable catalytic properties. Taking into account the promising electrocatalytic activity in the oxygen reduction reaction (ORR) demonstrated by nanoparticles of cobalt oxides [157], an attempt to produce such a material for the PEMFC electrodes by the PECVD method has been undertaken in our laboratory. The CoO_X-based films obtained from the $CpCo(CO)_2$ precursor (see: Sec. 4.3.1) were deposited on carbon paper substrate, and they were tested as the cathode in a hydrogen PEMFC (the anode was made of platinum). The preliminary results admittedly indicated the electrocatalytic activity of the films in the oxygen reduction reaction; however, it was far from the activity of Pt cathodes [17, 123]. Optimization of the conditions of plasma deposition and an enhanced procedure for the preparation of membrane electrode assemblies resulted in a significant improvement of the CoO_X electrocatalytic activity. Figure 17 presents current–voltage characteristics of the PEMFC with the cathode made of CoO_X deposited at various times (with various amounts of CoO_X) and Pt anode. The characteristic of the cell with both Pt electrodes is also shown. As can be seen, the cell with the Pt anode and CoO_X cathode is characterized by the open circuit voltage of 635 mV, which is already close to 963 mV obtained for the "pure" Pt cell [158]. Further progress in this area is expected, for example, by using doped CoO_X films and increasing the dispersion of Co_3O_4 nanoclusters.

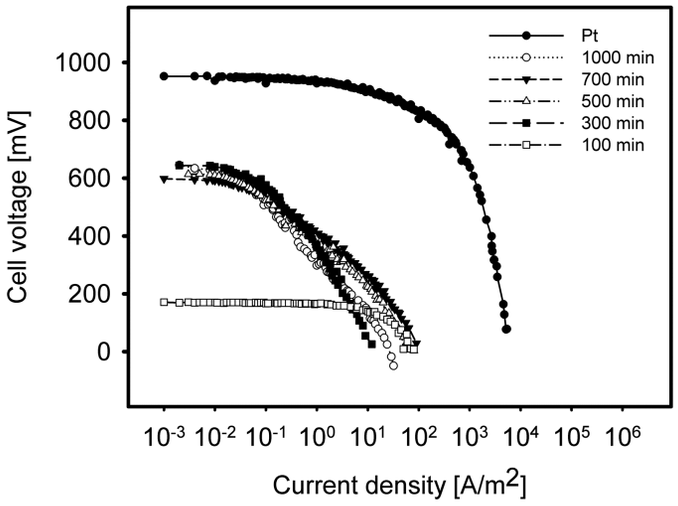


Figure 17. Current–voltage characteristics of PEMFC with the cathode of varying amounts of CoO_X deposit. The characteristic for the reference cell with both Pt electrodes is shown for comparison [158].

Very recently, we have obtained interesting results concerning the PEMFC, in which plasma-deposited FeO_X-based films were used as the cathode. The films have been deposited from $Fe(CO)_5$ (see: Sec. 4.3.2). An example of the preliminary results recorded for the fuel cell with such a cathode (and Pt anode) is shown in Figure 18. Although the results are far from expected, they point the way to further research in this area [150].

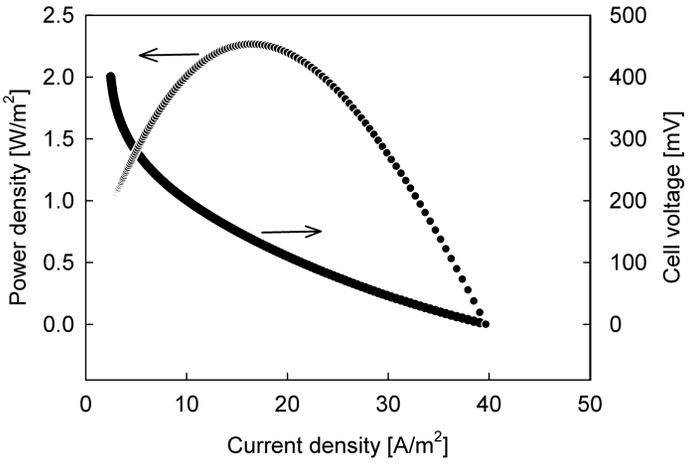


Figure 18. Power and potential versus current density for PEMFC with FeO_X cathode [150].

4.4.3. Water splitting systems

The most desirable method of hydrogen production, which represents a sustainable fuel of the future, is photoelectrochemical (PEC) splitting of water by visible light. A very important issue in the PEC hydrogen generation is the development of a high-performance photoelectrode that exhibits high efficiency in the conversion of solar energy into chemical energy, resistance to corrosion in aqueous environments, and low processing costs. However, after four decades of intensive research, since the first report on water photo-splitting [159], no material has been found to simultaneously satisfy all the criteria required for widespread PEC application. No wonder that a quest for new materials for photoelectrodes is still ongoing. The PECVD technique is also involved in this search [17].

Particular attention has recently been paid to FeO_X-based films (see: Sec. 4.3.2). Among iron oxides, hematite (α-Fe_2O_3) is considered as an attractive photoanode material, largely due to its abundance, chemical stability in aqueous environments, and light absorption in the visible range of the solar spectrum (E_g = 2.1–2.2 eV). However, the reported water-splitting efficiency of α-Fe_2O_3 is much lower (< 3.0 %) than the maximum theoretical value (~13 %), mainly due to the low absorption coefficient and slow reaction kinetics, resulting in a high carrier recombination rate and short hole diffusion length. Singh et al. [139] achieved the photocurrent density of about 1.1 mA/cm^2 at 0.9 V/SCE (with onset potential 0.6 V/SCE) for α-Fe_2O_3 films applied as a photoanode in 1M NaOH electrolyte (deposited from $Fe(CO)_5$). Naturally, this value depends on the used light intensity and development of the substrate surface, thus it is difficult to compare this particular result with those obtained in other laboratories. Nevertheless, it can be concluded that the films deposited in our laboratory from the same precursor under conditions that allow formation of γ-Fe_2O_3 nanoparticles reveal similar, if not better, photoactivity. For example, the onset potential is about 0.45 V/SCE.

A considerable improvement was observed in the photoactivity of α-Fe_2O_3 films treated by hydrogen plasma, which led to the formation of a complex structure of Fe_3O_4:α-Fe_2O_3 type. In

this case, enhanced photocurrent densities (3.5 mA/cm^2 at 1.8 V/RHE) and reduced photocurrent onset potentials (from 1.68V/RHEfor non-treated films to 1.28 V/RHE) were measured in 1M NaOH electrolyte [140].

In search for further opportunities to improve photocatalytic properties of FeO_X thin films, tuning of the system nano-organization and controlled tailoring of the chemical composition have been proposed. In particular, oriented columnar nanostructures offer the possibility of absorbing a significant fraction of light while providing short carrier transport distances to the electrolyte, thus minimizing recombination losses. Recently, columnar arrays of β-Fe_2O_3 showing a preferred (100) growth direction and highly porous structure have been successfully obtained in Ar/O_2 plasma by Barreca et al. [137]. The decoration of such columnar arrays with other transition metal oxides, such as cobalt oxide [149] and copper oxide [148], in the form of nanoparticles, might profitably suppress charge carrier recombination and improve Fe_2O_3 catalytic activity in water splitting. For example, the Fe_2O_3–Co_3O_4 heterostructure nanosystem reveals a photocurrent increase of 40% with respect to bare Fe_2O_3, which clearly proves that nanosystems produced with the involvement of PECVD are very promising [149].

Some interesting results have been obtained very recently in our laboratory for Ru^0/RuO_2 films produced by the PECVD (see: Sec. 4.2). In Figure 19, the photocurrent density (with subtracted dark current) measured under illumination from a 150 W Xe arc lamp equipped with an AM 1.5 filter, as a function of the applied voltage, is presented. As shown in the figure, the achieved value of the photocurrent is 9.1 mA/cm^2 at 0.6 V/SCE, which, compared with the results obtained in the same experimental system for Fe_2O_3 films (0.65 mA/cm^2 at 0.6 V/SCE) and Co_3O_4 films (0.48 mA/cm^2 at 0.6 V/SCE), is a very promising finding [142].

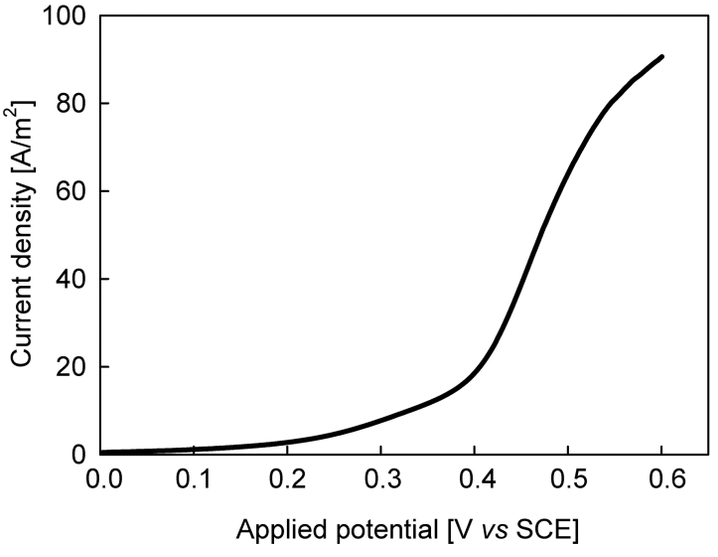


Figure 19. Photocurrent–voltage characteristic for Ru^0/RuO_2 photoanode prepared by PECVD (measurements in 1M NaOH electrolyte) [142].

5. Conclusions and outlook

I hope that after reading this chapter, the reader will no longer have any doubt that the enormous potential is hidden in the cold plasma technology. This technology gives us almost unlimited possibilities of modifying various materials and producing entirely new structures. This is particularly true with respect to the field of catalysis.

On one hand, the high-temperature processes such as decomposition of precursors, pyrolysis, calcination, reduction, and regeneration can be replaced by low-temperature plasma treatment, which minimizes problems caused by high temperature, such as aggregation, crystallite size growth, and sublimation, often leading to the creation of a completely different structure of the resulting catalyst. Generally, the conventional catalysts prepared with the involvement of cold plasma methods exhibit much higher activity, enhanced selectivity, and better stability. On the other hand, the cold plasma techniques, such as plasma sputtering and especially plasma polymerization (PECVD), have paved the way for the design at the molecular level and production of new advanced catalysts. Very thin films of precisely controlled molecular structure, 3D nanostructured systems, nanocomposites, all these put the cold plasma at the forefront of the twenty-first century methods of catalyst synthesis.

It is hard to imagine further progress in the construction of structured reactors without very thin catalytic films easily and cheaply deposited on precisely designed, sophisticated fillers designated for these reactors. The current development of hydrogen technologies also pins great hopes on new catalyst systems produced using the cold plasma. Although we are only at the beginning of the road, the results already obtained in the field of plasma-prepared catalytic electrodes for fuel cells and photocatalytic electrodes for PEC cells are very promising.

The ability to design new plasma nanomaterials possessing the desired catalytic properties and their preparation through controlled processes carried out in the cold plasma still pose a serious scientific challenge. As of now, the relation between cold plasma processes and the resulting structure and catalytic properties of deposited films is not entirely clear either. Further research in this field will undoubtedly lead to significant progress in science and provide attractive catalytic systems for technology.

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References

[1] Kizling MB, Järås SG. A review of the use of plasma techniques in catalyst preparation and catalytic reactions. Appl Catal A-Gen 1996;147:1–21.

[2] Liu CJ, Vissokov GP, Jang BWL. Catalyst preparation using plasma technologies. Catal Today 2002;72:173–84.

[3] Tyczkowski J, Kapica R. Cold plasma in the nanotechnology of catalysts. Pol J Chem Technol 2007;9:36–42.

[4] Kapoor A, Goyal SK, Bakhshi NN. Fischer–tropsch studies on a plasma-sprayed iron catalyst in a tube-wall reactor. Can J Chem Eng 1986;64:792–802.

[5] Dalai Ak, Bakhshi NN, Esmail MN. Conversion of syngas to hydrocarbons in a tube-wall reactor using Co–Fe plasma-sprayed catalyst: experimental and modeling studies. Fuel Process Technol 1997;51:219–38.

[6] Blanchard J, Abatzoglou N, Eslahpazir-Esfandabadi R, Gitzhofer F. Fischer-Tropsch synthesis in a slurry reactor using a nanoiron carbide catalyst produced by a plasma spray technique. Ind Eng Chem Res 2010;49:6948–55.

[7] Ismagilov ZR, Podyacheva OY, Solonenko OP, Pushkarev VV, Kuz'min VI, Ushakov VA, Rudina NA. Application of plasma spraying in the preparation of metal-supported catalysts. Catal Today 1999;51:411–7.

[8] Hinokuma S, Murakami K, Uemura K, Matsuda M, Ikeue K, Tsukahara N, Machida M. Arc plasma processing of Pt and Pd catalysts supported on γ-Al_2O_3 powders. Top Catal 2009;52:2108–11.

[9] Pristavita R, Meunier JL, Berk D. Carbon nano-flakes produced by an inductively coupled thermal plasma for catalyst applications. Plasma Chem. Plasma Process 2011;31:393–403.

[10] Maunier JL, Mendoza-Gonzalez NY, Prostavita R, Binny D, Berk D. Two-dimensional geometry control of graphene nanoflakes produced by thermal plasma for catalyst applications. Plasma Chem Plasma Process 2014;34:505–21.

[11] Wong FF, Lin CM, Chang CP, Huang JR, Yeh MY, Huang JJ. Recovery and reduction of spent nickel oxide catalyst via plasma sintering technique. Plasma Chem Plasma Process 2006;26:585–95.

[12] Wong FF, Chiang KC, Chen CY, Chen KL, Huang JJ, Yeh MY. Recovery and reduction of spent alumina-supported cobalt-molybdenum oxide catalyst via plasma sintering technique. Plasma Chem Plasma Process 2008;28:353–63.

[13] Seo JH, Lee MY, Kim JS. Radio-frequency thermal plasma preparation of nano-sized Ni catalysts supported on MgO nano-rods for partial oxidation of methane. Surf Coat Tech 2013;228:S91–6.

[14] Nehe P, Sivakumar G, Kumar S. Solution precursor plasma spray (SPPS) technique of catalyst coating for hydrogen production in a single channel with cavities plate type methanol based microreformer. Chem Eng J 2015;277:168–75.

[15] Witvrouwen T, Paulussen S, Selt B. The use of non-equilibrium plasmas for the synthesis of heterogeneous catalysts. Plasma Process Polym 2012;9:750–60.

[16] Kołodziej A, Łojewska J, Tyczkowski J, Jodłowski P, Redzynia W, Iwaniszyn M, Zapotoczny S, Kuśtrowski P. Coupled engineering and chemical approach to the design of a catalytic structured reactor for combustion of VOCs: Cobalt oxide catalyst on knitted wire gauzes. Chem Eng J 2012;200–202:329–37.

[17] Tyczkowski J. Cold plasma – a promising tool for the development of electrochemical cells. In: Shao Y, editor. Electrochemical Cells – New Advances in Fundamental Researches and Applications. Rijeka, Croatia: InTech; 2012. pp. 105–138.

[18] Chen MH, Chu W, Dai XY, Zhang XW. New palladium catalysts prepared by glow discharge plasma for the selective hydrogenation of acetylene. Catal Today 2004;89:201–4.

[19] Liu CJ. Yu K, Zhang YP, Zhu X, He F, Eliasson B. Characterization of plasma treated Pd/HZSM-5 catalyst for methane combustion. Appl Catal B-Environ 2004;47:95–100.

[20] Zhu X, Yu K, Li J, Zhang YP, Xia Q, Liu CJ. Thermogravimetric analysis of coke formation on plasma-treated Mo-Fe/HZSM-5 catalyst during non-oxidative aromatization of methane. React Kinet Catal Lett 2006;87:93–9.

[21] Legrand JC, Diamy AM, Riahi G, Randriamanantenasoa Z, Polisset-Thfoin M, Fraissard J. Application of a dihydrogen afterglow to the preparation of zeolite-supported metallic nanoparticles. Catal Today 2004;89:177–82.

[22] Liu CJ, Cheng DG, Zhang YP, Yu KL, Xia Q, Wang JG, Zhu XL. Remarkable enhancement in the dispersion and low-temperature activity of catalysts prepared via novel plasma reduction-calcination method. Catal Surv Asia 2004;8:111–8.

[23] Zhang YP, Ma PS, Zhu X, Liu CJ, Shen Y. A novel plasma-treated Pt/NaZSM-5 catalyst for NO reduction by methane. Catal Commun 2004;5:35–9.

[24] Zhu X, Huo PP, Zhang YP, Liu CJ. Characterization of argon glow discharge plasma reduced Pt/Al_2O_3 catalyst. Ind Eng Chem Res 2006;45:8604–9.

[25] Brüser V, Savastenko N, Schmuhl A, Junke H, Herrmann I, Bogdanoff P, Schröder K. Plasma modification of catalysts for cathode reduction of hydrogen peroxide in fuel cells. Plasma Process Polym 2007;4:594–8.

[26] Cheng DG, Okumura K, Xie Y, Liu CJ. Stability test and EXAFS characterization of plasma prepared Pd/HZSM-5 catalyst for methane combustion. Appl Surf Sci 2007;254:1506–10.

[27] Lihong H, Wei C, Junqiang X, Jingping H, Min Y. Effect of glow discharge plasma on rhodium-based catalyst for oxygenates synthesis. Front Chem Eng China 2007;1:16–9.

[28] Zhu X, Huo P, Zhang YP, Cheng DG, Liu CJ. Structure and reactivity of plasma treated Ni/Al_2O_3 catalyst for CO_2 reforming of methane. Appl Catal B-Environ 2008;81:132–40.

[29] Chu W, Wang LN, Chernavskii PA, Khodakov AY. Glow-discharge plasma-assisted design of cobalt catalysts for Fischer-Tropsch synthesis. Angew Chem Int Edit 2008;47:5052–55.

[30] Liu G, Chu W, Shi X, Dai X, Yin Y. Plasma-assisted preparation of Ni/SiO_2 catalyst using atmospheric high frequency cold plasma jet. Catal Commun 2008;9:1087–91.

[31] Xu H, Chu W, Shi L, Deng S, Zhang H. Effects of glow discharge plasma on Cu–Co–Al-based supported catalysts for higher alcohol synthesis. React Kinet Catal Lett 2009;97:243–7.

[32] Li Y, Jang BWL. Investigation of calcination and O_2 plasma treatment effects on TiO_2-supported palladium catalysts. Ind Eng Chem Res 2010;49:8433–8.

[33] Huang C, Bai S, Lv J, Li Z. Characterization of silica-supported cobalt catalysts prepared by decomposition of nitrates using dielectric-barrier discharge plasma. Catal Lett 2011;141:1391–8.

[34] Zhang MB, Zhu XL, Liang X, Wang Z. Preparation of highly efficient Au/C catalysts for glucose oxidation via novel plasma reduction. Catal Commun 2012;25:92–5.

[35] Kuai PY, Liu CJ, Huo PP. Characterization of CuO-ZnO catalust prepared by decomposition of carbonates using dielectric-barrier discharge plasma. Catal Lett 2009;129:493–8.

[36] Hua W, Jin L, He X, Liu J, Hu H. Preparation of Ni/MgO catalyst for CO_2 reforming of methane by dielectric-barrier discharge plasma. Catal Commun 2010;11:968–72.

[37] Yan X, Liu Y, Zhao B, Wang Z, Wang Y, Liu CJ. Methanation over Ni/SiO_2: effect of the catalyst preparation methodologies. Int J Hydrogen Energ 2013;38:2283–91.

[38] Li Y, Wei Z, Wang Y. Ni/MgO catalyst prepared via dielectric-barrier discharge plasma with improved catalytic performance for carbon dioxide reforming of methane. Front Chem Sci Eng 2014;8:133–40.

[39] Shi P, Liu CJ. Characterization of silica supported nickel catalyst for methanation with improved activity by room temperature plasma treatment. Catal Lett 2009;133:112–8.

[40] Chen MH, Chu W, Zhu JJ, Dong L. Plasma assisted preparation of cobalt catalysts by sol–gel method for methane combustion. J Sol-Gel Sci Technol 2008;47:354–9.

[41] Teng F, Li M, Gao C, Zhang G, Zhang P, Wang Y, Chen L, Xie E. Preparation of block TiO_2 by hydrogen plasma assisted chemical vapor deposition and its photocatalytic activity. Appl Catal B-Environ 2014;148/149:339–43.

[42] Cheng DG. Plasma decomposition and reduction in supported metal catalyst preparation. Catal Surv Asia 2008;12:145–51.

[43] Liu C, Zou J, Yu K, Cheng DG, Han Y, Zhan J, Ratanatawanate C, Jang BWL. Plasma application for more environmentally friendly catalyst preparation. Pure Appl Chem 2006;78:1227–38.

[44] Cheng DG, Zhu X. Reduction of Pd/HZSM-5 using oxygen glow discharge plasma for a highly durable catalyst preparation. Catal Lett 2007;118:260–3.

[45] Jung B, Helleson M, Shi C, Rondinone A, Schwartz V, Liang C, Overbury S. Characterization of Al_2O_3 supported nickel catalysts derived from RF non-thermal plasma technology. Top Catal 2008;49:145–52.

[46] Médard N, Soutif JC, Lado I, Esteyries C, Poncin-Epaillard F. Synthesis and characterization of new supported metallocene catalysts using a cold plasma treatment: application to molecular mechanics and dynamics computational modeling. Macromol Chem Phys 2001;202:3606–16.

[47] Lopez LC, Buonomenna MG, Fontananova E, Iacoviello G, Drioli E, d'Agostino R, Favia P. A new generation of catalytic poly(vinylidene fluoride) membranes: Coupling plasma treatment with chemical immobilization of tungsten-based catalysts. Adv Funct Mater 2006;16:1417–24.

[48] Lopez LC, Buonomenna MG, Fontananova E, Drioli E, Favia P, d'Agostino R. Immobilization of tungsten catalysts on plasma modified membranes. Plasma Process Polym 2007;4:326–33.

[49] Liu X, Mou CY, Lee S, Li Y, Secrest J, Jang BWL. Room temperature O_2 plasma treatment SiO_2 supported Au catalysts for selective hydrogenation of acetylene in the presence of large excess of ethylene. J Catal 2012;285:152–9.

[50] Korovchenko P, Renken A, Kiwi-Misker L. Microwave plasma assisted preparation of Pd-nanoparticles with controlled dispersion on woven activated carbon fibres. Catal Today 2005;102/103:133–41.

[51] Chen J, Zhu ZH, Ma Q, Li L, Rudolph V, Lu GQ. Effects of pre-treatment in air microwave plasma on the structure of CNTs and the activity of Ru/CNTs catalysts for ammonia decomposition. Catal Today 2009;148:97–102.

[52] Chetty R, Maniam KK, Schuhmann W, Muhler M. Oxygen-plasma-functionalized carbon nanotubes as supports for platinum-ruthenium catalysts applied in electrochemical methanol oxidation. Chem Plus Chem 2015;80:130–5.

[53] Wirth S, Harnisch F, Quade A, Brüser M, Brüser V, Schröder U, Savastenko NA. Enhanced activity of non-noble metal electrocatalysts for the oxygen reduction reaction using low temperature plasma treatment. Plasma Process Polym 2011;8:914–22.

[54] Gao JS, Umeda K, Uchino K, Nakashima H, Muroaka K. Plasma breaking of thin films into nano-sized catalysts for carbon nanotube synthesis. Mater Sci Eng 2003;A352:308–13.

[55] Gao JS, Umeda K, Uchino K, Nakashima H, Muroaka K.. Control of sizes and densities of nano catalysts for nanotube synthesis by plasma breaking method. Mater Sci Eng 2004;B107:113–8.

[56] Chang SC, Lin TC, Li TS, Huang SH. Carbon nanotubes grown from nickiel catalyst prepared with H_2/N_2 plasma. Microelectron J 2008;39:1572–5.

[57] Jian SR. Effects of H_2 plasma pretreated Ni catalysts on the growth of carbon nanotubes. Mater Chem Phys 2009;115:740–3.

[58] Lee SH, Kwak EH, Kim HS, Lee SW, Jeong GH. Evolution of gold thin films to nanoparticles using plasma ion bombardment and their use as a catalyst for carbon nanotube growth. Thin Solid Films 2013;547:188–92.

[59] Zhang C, Xie R, Chen B, Yang J, Zhong G, Robertson J. High density carbon nanotube growth using a plasma pretreated catalyst. Carbon 2013;53:339–45.

[60] Li ZH, Tian SX, Wang HT, Tian HB. Plasma treatment of Ni catalyst via a corona discharge. J Mol Catal A-Chem 2004;211:149–53.

[61] Zhu YR, Li ZH, Zhou YH, Lv J, Wang HT. Plasma treatment of Ni and Pt catalysts for partial oxidation of methane. React Kinet Catal Lett 2006;87:33–41.

[62] Li K, Tang X, Yi H, Ning P, Xiang Y, Wang J, Wang C, Peng X. Research on manganese oxide catalysts surface pretreated with non-thermal plasma for NO catalytic oxidation capacity enhancement. Appl Surf Sci 2013;264:557–62.

[63] Tang X, Li K, Yi H, Ning P, Xiang Y, Wang J, Wang C. MnOx catalysts modified by nonthermal plasma for NO catalytic oxidation. J Phys Chem C 2012;116:10017–28.

[64] Shi C, Hoisington R, Jang BWL. Promotion effects of air and H_2 nonthermal plasmas on TiO_2 supported Pd and Pd–Ag catalysts for selective hydrogenation of acetylene. Ind Eng Chem Res 2007;46:4390–5.

[65] Li Y, Jang BWL. Non-thermal RF plasma effects on surface properties of Pd/TiO_2 catalysts for selective hydrogenation of acetylene. Appl Catal A-Gen 2011;392:173–9.

[66] Yi H, Zhao S, Tang X, Song C, Gao F, Zhang B, Wang Z. Low-temperature hydrolysis of carbon disulfide using the Fe–Cu/AC catalyst modified by non-thermal plasma. Fuel 2014;128:268–73.

[67] Feng Y, Zheng X. Plasma-enhanced catalytic CuO nanowires for CO oxidation. Nano Lett 2010;10:4762–6.

[68] Gao F, Liu B, Sun W, Wu Y, Dong L. The influence of microwave plasma pretreated CuO/TiO_2 catalysts in NO + CO reaction. Catal Today 2011;175:34–9.

[69] Kim HH, Tsubota S, Daté M, Ogata A, Futumura S. Catalyst regeneration and activity enhancement of Au/TiO_2 by atmospheric pressure nonthermal plasma. Appl Catal A-Gen 2007;329:93–8.

[70] Yang X, Kimmel YC, Fu J, Koel BE, Chen JG. Activation of tungsten carbide catalysts by use of an oxygen plasma pretreatment. ACS Catal 2012;2:765–9.

[71] Rossnagel SM, Cuomo JJ, Westwood WD, editors. Handbook of Plasma Processing Technology; Fundamentals, Etching, Deposition, and Surface Interactions. Park Ridge, New Jersey, USA: Noyes Publ; 1990. 523 p.

[72] Thomann AL, Rozenbaum JP, Brault P, Andreazza-Vignolle C, Andreazza P. Pd nanoclusters grown by plasma sputtering deposition on amorphous substrates. Appl Surf Sci 2000;158:172–83.

[73] Estrada W, Fantini MCA, de Castro SC, Polo da Fonseca CN, Gorenstein A. Radio frequency sputtered cobalt oxide coating: Structural, optical and electrochemical characterization. J Appl Phys 1993;74:5835–41.

[74] Witham CK, Chun W, Valdez TI, Narayanan SR. Performance of direct methanol fuel cells with sputter-deposited anode catalyst layers. Electrochem Solid-State Lett 2000;3:497–500.

[75] Brault P, Thomann AL, Rozenbaum JP, Cormier JM, Lefaucheux P, Andreazza C, Andreazza P. The use of plasma in catalysis: catalyst preparation and hydrogen production. Ann Chim Sci Mat 2001;26:69–77.

[76] Thomann AL, Rozenbaum JP, Brault P, Andreazza C, Andreazza P, Rousseau B, Estrade-Szwarckopf H, Berthet A, Bertolini JC, Cadera Santos Aires FJ, Monnet F, Mirodatos C, Charles C, Boswell R. Plasma synthesis of catalytic thin films. Pure Appl Chem 2002;74:471–4.

[77] Park KW, Choi JH, Ahn KS, Sung YE. PtRu alloy and PtRu–WO_3 nanocomposite electrodes for methanol electrooxidation fabricated by a sputtering deposition method. J Phys Chem B 2004;108:5989–94.

[78] Whitacre JF, Valdez T, Narayanan SR. Investigation of direct methanol fuel cell electrocatalysts using a robust combinatorial technique. J Electrochem Soc 2005;152:A1780–9.

[79] Alvisi M, Galtieri G, Giorgi L, Giorgi R, Serra E, Signore MA. Sputter deposition of Pt nanoclusters and thin films on PEM fuel cell electrodes. Surf Coat Tech 2005;200:1325–9.

[80] Saha MS, Gullá AF, Allen RJ, Mukerjee S. High performance polymer electrolyte fuel cells with ultra-low Pt loading electrodes prepared by dual ion-beam assisted deposition. Electrochim Acta 2006;51:4680–92.

[81] Whitacre JF, Valdez TI, Narayanan SR. A high-throughput study of PtNiZr catalysts for application in PEM fuel cells. Electrochim Acta 2008;53:3680–9.

[82] Xinyao Y, Zhongqing J, Yuedong M. Preparation of anodes for DMFC by co-sputtering of platinum and ruthenium. Plasma Sci Technol 2010;12:224–9.

[83] Ohnishi R, Katayama M, Kakanabe K, Kubota J, Domen K. Niobium-based catalysts prepared by reactive radio-frequency magnetron sputtering and arc plasma methods as non-noble metal cathode catalysts for polymer electrolyte fuel cells. Electrochim Acta 2010;55:5393–400.

[84] Mougenot M, Caillard A, Simoes M, Baranton S, Coutanceau C, Brault P. PdAu/C catalysts prepared by plasma sputtering for the electro-oxidation of glycerol. Appl Catal B-Environ 2011;107:372–9.

[85] Fofana D, Natarajan SK, Benard P, Hamelin J. High performance PEM fuel cell with low platinum loading at the cathode using magnetron sputter deposition. ISRN Electrochem 2013;2013:ID 174834, 6 pages.

[86] Caillard A, Charles C, Ramdutt D, Boswell R, Brault P. Effecy of Nafion and platinum content in a catalyst layer processed in a radio frequency helicon plasma system. J Phys D Appl Phys 2009;42:ID 045207, 9 pages

[87] Brault P, Caillard A, Thomann AL, Mathias J, Charles C, Boswell RW, Escribano S, Durand J, Sauvage T. Plasma sputtering deposition of platinum into porous fuel cell electrodes. J Phys D Appl Phys 2004;37:3419–23.

[88] Caillard A, Brault P, Mathias J, Charles C, Boswell RW, Sauvage T. Deposition and diffusion of platinum nanoparticles in porous carbon assisted by plasma sputtering. Surf Coat Tech 2005;200:391–4.

[89] Dilonardo E, Milella A, Cosma P, d'Agostino R, Palumbo F. Plasma deposited electrocatalytic films with controlled content of Pt nanoclusters. Plasma Process Polym 2011;8:452–8.

[90] Walter C, Brüser V, Quade A, Weltmann KD. Structural investigations of composites produced from copper and polypyrrole with a dual PVD/PE-CVD process. Plasma Process Polym 2009;6:803—12.

[91] Walter C, Kummer K, Vyalikh D, Brüser V, Quada A, Weltmann KD. Using a dual plasma process to produce cobalt-polypyrrole catalysts for the oxygen reduction reaction in fuel cells. I. Characterization of the catalytic activity and surface structure. J Electrochem Soc 2012;159:F494—500.

[92] Walter C, Kummer K, Vyalikh D, Brüser V, Weltmann KD. Tuning the process gas in a dual plasma process to enhanced the performance of cobalt–polypyrrole catalysts for the oxygen reduction reaction in fuel cells. J Electrochem Soc 2013;160:F1088—95.

[93] Walter C, Kummer K, Vyalikh D, Brüser V, Weltmann KD. Iron–polypyrrole catalyst for the oxygen reduction in proton exchange membrane fuel cells produced with a dual plasma process using varying magnetron powers and process gases. Plasma Chem Plasma Process 2014;34:785—99.

[94] Tyczkowski J. Electrical and optical properties of plasma polymers. In: Biederman H, editor. Plasma Polymer Films. London: Imperial College Press; 2004. pp. 143—216.

[95] Suhr H, Etspüler A, Feurer E, Oehr C. Plasma-deposited metal-containing polymer films. Plasma Chem Plasma Process 1988;8:9—17.

[96] Feurer E, Suhr H. Thin palladium films prepared by metal-organic plasma-enhanced chemical vapour deposition. Thin Solid Films 1988;157:81—6.

[97] Etspüler A, Suhr H. Deposition of thin rhodium films by plasma-enhanced chemical vapor deposition. Appl Phys A 1989;48:373—5.

[98] Feurer E, Kraus S, Suhr H. Plasma chemical vapor deposition of thin platinum films. J Vac Sci Technol A 1989;7:2799—802.

[99] Doblhofer K. Electrodes covered with thin, permeable polymer films. Electrochim Acta 1980;25:871—8.

[100] Doblhofer K, Eiselt I. Electrochemical performance of fixed-charge polymer films prepared on electrodes by plasma polymerization. Thin Solid Films 1984;118:181—5.

[101] Song SJ, Jung KW, Cho MD, Yang EJ, Sim HJ, Kim MY, Jang HG, Seo G, Cho DL. Preparation of amine-immobilized solid base catalysts by plasma polymerization of 1,2-diaminocyclohexane. Appl Catal A-Gen 2012;429/430:85—91.

[102] Guyon C, Barkallah A, Rousseau F, Giffard K, Morvan D, Tatoulian M. Deposition of cobalt oxide thin films by plasma-enhanced chemical vapour deposition (PECVD) for catalytic applications. Surf Coat Tech 2011;206:1673—9.

[103] Chen GL, Guyon C, Zhang ZX, Da Silva B, Da Costa P, Ognier S, Bonn D, Tatoulian M. Catkin liked nano-Co_3O_4 catalyst built-in organic microreactor by PEMOCVD method for trace CO oxidation at room temperature. Microfluid Nanofluid 2014;16:141—8.

[104] Witvrouwen T, Dijkmans J, Paulussen S, Selt B. Optimization of the synthesis conditions of a DBD plasma reactor for the synthesis of hybrid silica-based catalysts. Plasma Process Polym 2014;11:464—71.

[105] Dittmar A, Hoang DL, Martin A. TPR and XPS characterization of chromia–lanthana–zirconia catalyst prepared by impregnation and microwave plasma enhanced chemical vapour deposition methods. Thermochim Acta 2008;470:40—6.

[106] Dittmar A, Herein D. Microwave plasma assisted preparation of disperse chromium oxide supported catalysts: adsorption and decomposition of chromium acetylacetonate. Surf Coat Tech 2009;203:992—7.

[107] Laurent-Brocq M, Job N, Eskenazi D, Pireaux JJ. Pt/C catalyst for PEM fuel cells: Control of Pt nanoparticles characteristics through a novel plasma deposition method. Appl Catal B-Environ 2014;147:453—63.

[108] George SM. Atomic layer deposition: an overview. Chem Rev 2010;110:111—31.

[109] O'Neill BJ, Jackson DHK, Lee J, Canlas C, Stair PC, Marshall CL, Elam JW, Kuech TF, Dumesic JA, Huber GW. Catalyst design with atomic layer deposition. ACS Catal 2015;5:1804—25.

[110] Koyano G, Watanabe H, Okuhara T, Misono M. Structure and catalysis of cobalt oxide overlayers prepared on zirconia by low-temperature-plasma oxidation. J Chem Soc Faraday T 1996;92:3425—30.

[111] Ruddick VJ, Badyal PS. Nonequilibrium plasma activation of supported Cr(III) Phillips catalyst precursors. J Phys Chem B 1997;101:9240—3.

[112] Dhar R, Petrow PD, Liddell KNC, Ming Q, Moeller TM, Osman MA. Plasma-enhanced metal-organic chemical vapor deposition (PEMOCVD) of catalytic coatings for fuel cell reformers. IEEE T Plasma Sci 2005;33:138—46.

[113] Dhar R, Petrow PD, Liddell KNC, Ming Q, Moeller TM, Osman MA. Synthesis of Pt/ZrO_2 catalyst on Fecralloy substrates using composite plasma-polymerized films. IEEE T Plasma Sci 2005;33:2035—45.

[114] Kapica R, Redzynia W, Tyczkowski J. Characterization of palladium-based thin films prepared by plasma-enhanced metalorganic chemical vapor deposition. Mater Sci-Medzg 2012;18:128—31.

[115] Ten Eyck GA, Senkevich JJ, Tang F, Liu D, Pimanpang S, Karaback T, Wang GC, Lu TM, Jezewski C, Lanford WA. Plasma-assisted atomic layer deposition of palladium. Chem Vapor Depos 2005;11:60—6.

[116] Weber MJ, Mackus AJM, Verheijen MA, Longo V, Bol AA, Kessels WMM. Atomic layer deposition of highly-purity palladium films from $Pd(hfac)_2$ and H_2 and O_2 plasmas. J Phys Chem C 2014;118:8702—11.

[117] Wojcik H, Junige M, Bartha W, Albert M, Neumann V, Merkel U, Peeva A, Gluch J, Menzel S, Munnik F, Liske R, Utess D, Richter I, Klein C, Engelmann HJ, Ho P, Hossbach C, Wenzel C. Physical characterization of PECVD and PEALD Ru(-C) films and comparison with PVD ruthenium film properties. J Electrochem Soc 2012;159:H166—76.

[118] Park T, Choi D, Choi H, Jeon H. The properties of Ru films deposited by remote plasma atomic layer deposition on Ar plasma-treated SiO_2. Phys Status Solidi A 2012;209:302—5.

[119] Dittmar A, Kosslick H, Müller JP, Pohl MM. Characterization of cobalt oxide supported on titania prepared by microwave plasma enhanced chemical vapor deposition. Surf Coat Tech 2004;182:35—42.

[120] Barreca D, Devi A, Fischer RA, Bekermann D, Gasparotto A, Gavagnin M, Maccato C, Tondello E, Bontempi E, Depero LE, Sada C. Strongly oriented Co_3O_4 thin films on MgO(100) and $MgAl_2O_4$(100) substrates by PE-CVD. Cryst Eng Comm 2011;13:3670–3.

[121] Donders ME, Knops HCM, Sanden MCM, van deKessels WMM, Notten PHL. Remote plasma atomic layer deposition of Co_3O_4 thin films. J Electrochem Soc 2011;158:G92—6.

[122] Tyczkowski J, Kapica R, Łojewska J. Thin cobalt oxide films for catalysis deposited by plasma-enhanced metal-organic chemical vapor deposition. Thin Solid Films 2007;515:6590—5.

[123] Tyczkowski J. New materials for innovative energy systems produced by cold plasma technique. Funct Mater Lett 2011;4:341—4.

[124] Kapica R, Redzynia W, Kozanecki M, Chehimi MM, Sielski J, Kuberski SM, Tyczkowski J. Plasma deposition and characterization of copper-doped cobalt oxide nanocatalysts. Mater Sci-Medzg 2013;19:270—6.

[125] Battiston GA, Gerbasi R, Gregori A, Porchia M, Cattarin S, Rizzi GA. PECVD of amorphous TiO_2 thin films: Effect of growth temperature and plasma gas composition. Thin Solid Films 2000;371:126—31.

[126] da Cruz NC, Rangel EC, Wang J, Trasferetti BC, Davanzo CU, Castro SGC, de Moraes AB. Properties of titanium oxide films obtained by PECVD. Surf Coat Tech 2000;126:123—30.

[127] Maeda M, Watanabe T. Evaluation of photocatalytic properties of titanium oxide films prepared by plasma-enhanced chemical vapor deposition. Thin Solid Films 2005;489:320—4.

[128] Randeniya LK, Bendavid A, Martin PJ, Preston EW. Photoelectrochemical and structural properties of TiO_2 and N-doped TiO_2 thin films synthesized using pulsed direct current plasma-activated chemical vapor deposition. J Phys Chem C 2007;111:18334—40.

[129] Cho DL, Min H, Kim JH, Cha GS, Kim GS, Kim BH, Ohk SH. Photocatalytic characteristics of TiO_2 thin films deposited by PECVD. J Ind Eng Chem 2007;13:434—7.

[130] Borras A, Sanchez-Valencia JR, Widmer R, Rico VJ, Justo Angel, Gonzalez-Elipe AR. Growth of crystalline TiO_2 by plasma enhanced chemical vapor deposition. Cryst Growth Des 2009;9:2868—76.

[131] Borras A, Sanchez-Valencia JR, Garrido-Molinero J, Barranco A, Gonzalez-Elipe AR. Porosity and microstructure of plasma deposited TiO_2 thin films. Micropor Mesopor Mat 2009;118:314—24.

[132] Karches M, Morstein M, von Rohr PR, Pozzo RL, Giombi JL, Baltanás MA. Plasma-CVD-coated glass beads as photocatalyst for water decontamination. Catal Today 2002;72:267—79.

[133] Sobczyk-Guzenda A, Owczarek S, Szymanowski H, Gazicki-Lipman M. Amorphous and crystalline TiO_2 coatings synthesized with the RF PECVD technique from metal-organic precursor. Vacuum 2015;117:104—11.

[134] Kment S, Kluson P, Zabova H, Churpita A, Chichina M, Cada M, Gregora I, Krysa J, Hubicka Z. Atmospheric pressure barrier torch discharge and its optimization for flexible deposition of TiO_2 thin coatings on various surfaces. Surf Coat Tech 2009;204:667—75.

[135] Cho BO, Wang J, Chang JP. Metalorganic precursor decomposition and oxidation mechanisms in plasma-enhanced ZrO_2 deposition. J Appl Phys 2002;92:4238—44.

[136] Fujii E, Torii H, Tomozawa A, Takayama R, Hirao T. Iron oxide films with spinel, corundum and bixbite structure prepared by plasma-enhanced metalorganic chemical vapor deposition. J Cryst Growth 1995;151:134—9.

[137] Barreca D, Carraro G, Gasparotto A, Maccato C, Sada C, Singh AP, Mathur S, Mettenbörger A, Bontempi E, Depero LE. Columnar Fe_2O_3 arrays via plasma-enhanced growth: Interplay of fluorine substitution and photoelectrochemical properties. Int J Hydrogen Energ 2013;38:14189—99.

[138] Ramachandran RK, Dendooven J, Detavernier C. Plasma enhanced atomic layer deposition of Fe_2O_3 thin films. J Mater Chem A 2014;2:10662—7.

[139] Singh AP, Mettenbörger A, Golus P, Mathur S. Photoelectrochemical properties of hematite films grown by plasma enhanced chemical vapor deposition. Int J Hydrogen Energ 2012;37:13983—8.

[140] Mettenbörger A, Singh T, Singh AP, Järvi TT, Moseler M, Valldor M, Mathur S. Plasma-chemical reduction of iron oxide photoanodes for efficient solar hydrogen production. Int J Hydrogen Energ 2014;39:4828—35.

[141] Redzynia W, Balcerzak J, Sielski J, Kierzkowska-Pawlak H, Tyczkowski J. Promising PEMOCVD cobalt and ruthenium oxide layers for CO_2 methanation process. In: Tamulevicius S, editor. Advanced Materials and Technologies 2015; 27-31 August 2015; Palanga, Lithuania. Kaunas: Kaunas Univ Technol; 2015. p. 58.

[142] Marchwicka M, Jóźwiak Ł, Tyczkowski J. Plasma deposited Ru-based thin films for photoelectrochemical water splitting. Mater Sci-Medzg: submitted to editor.

[143] Lee SY, Park SJ. TiO_2 photocatalyst for water treatment applications. J Ind Eng Chem 2013;19:1761—9.

[144] Martinu L, Zabeida O, Klemberg-Sapieha JE. Plasma-enhanced chemical vapor deposition of functional coatings. In: Martin PM, editor. Handbook of Deposition Technologies for Films and Coatings: Science, Applications and Technology.Kidlington, Oxford, UK: Elsevier; 2010. pp. 392—465.

[145] Doblhofer K, Dürr W. Polymer-metal composite thin films on electrodes. J Electrochem Soc 1980;127:1041—4.

[146] Morosoff N, Patel DL, Lugg PS, Crumbliss AL. Chemical properties of metallated plasma polymers. J Appl Polym Sci: Appl Polym Symp 1984;38:83—98.

[147] Fujii E, Torii H, Tomozawa A, Takayama R, Hirao T. Preparation of cobalt oxide films by plasma-enhanced metalorganic chemical vapour deposition. J Mater Sci 1995;30:6013—8.

[148] Carraro G, Gasparotto A, Maccato C, Bontempi E, Bilo F, Peeters D, Sada, C, Barreca D. A plasma-assisted approach for the controlled dispersion of CuO aggregates into β iron(III) oxide matrices. Cryst Eng Comm 2014;16:8710—6.

[149] Carraro G, Maccato C, Gasparotto A, Kaunisto K, Sada C, Barreca D. Plasma-assisted fabrication of Fe_2O_3–Co_3O_4 nanomaterials as anodes for photoelectrochemical water splitting. Plasma Process Polym 2015;DOI: 10.1002/ppap.201500106.

[150] Jóźwiak Ł, Marchwicka M, Kazimierski P, Tyczkowski J. Plasma deposited thin films of iron oxide as oxygen reduction electrocatalysts in proton exchange membrane fuel cells. Mater Sci-Medzg: submitted to editor.

[151] Bartolome L, Imran M, Lee KG, Sangalang A, Ahn JK, Kim DH. Superparamagnetic γ-Fe_2O_3 nanoparticles as an easily recoverable catalyst for the chemical recycling of PET. Green Chem 2014;16:279—86.

[152] Lopatin S, Mikenin P, Pisarev D, Baranov D, Zazhigalov S, Zagoruiko A. Pressure drop and mass transfer in the structured cartridges with fiber-glass catalyst. Chem Eng J 2015;282:58–65.

[153] Łojewska J, Kołodziej A, Łojewski T, Kapica R, Tyczkowski J. Cobalt catalyst deposited on metallic microstructures for VOC combustion: Preparation by non-equilibrium plasma. Catal Commun 2008;10:142—5.

[154] Łojewska J, Kołodziej A, Kapica R, Knapik A, Tyczkowski J. In search for active non-precious metal catalyst for VOC combustion: evaluation of plasma deposited Co and Co/Cu oxide catalysts on metallic structured carriers. Catal Today 2009;147S:S94—8.

[155] Łojewska J, Kołodziej A, Łojewski T, Kapica R, Tyczkowski J. Structured cobalt oxide catalyst for VOC combustion. Part I: Catalytic and engineering correlations. Appl Catal A-Gen 2009;366:206—11.

[156] Tyczkowski J, Kapica R, Łojewska J, Kołodziej A. Method for obtaining a thin layer of catalyst material on substrates made of electrically conductive material. Patent. 2014;PL217586.

[157] Manzoli M, Boccuzzi F. Characterisation of Co-based electrocatalytic materials for O_2 reduction in fuel cells. J Power Sources 2005;145:161—8.

[158] Kazimierski P, Jóźwiak Ł, Sielski J, Tyczkowski J. Cobalt oxide-based catalysts deposited by cold plasma for proton exchange membrane fuel cells. Thin Solid Films 2015;594:5–11.

[159] Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. Nature 1972;238:37—8.

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