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Cold Plasma – A Promising Tool for the Development of Electrochemical Cells

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1. Introduction

The growing concern over the environment on a global basis is driving extensive research into new materials for next generation of clean, efficient, alternative energy systems, to a large extent based on various types of electrochemical cells. An especially useful method that has paved the way to novel materials with unique properties, which cannot be fabricated by other methods, is the cold plasma technology. Both integrally new materials in the form of thin films with unusual molecular structure and conventional materials modified by cold plasma, which reveal surprising surface properties, can be prepared in this way. Some of these materials turned out to be very interesting for the innovative electrochemical cells.

In this Chapter, a brief review of investigations performed on materials produced by the cold plasma technology and their testing in electrochemical cells, such as fuel cells, rechargeable cells and related devices as solar cells and water splitting systems, is presented. Some attention is paid to research conducted in our laboratory.[1] Recent results of our studies on plasma deposited thin films of nanocatalysts based on metal oxides, such as cobalt and cupper oxides, which have been tested as electrodes for fuel cells, are discussed in more detail. Our efforts directed towards the development of new materials for solar cells and water splitting systems are also mentioned. However, before turning to the details of these issues, we should first familiarize ourselves, even cursory, with the cold plasma technology.

2. What is the cold plasma?

As it is known, in the Universe, matter exists in four different states from the molecular interrelations point of view, namely: solid, liquid, gas and plasma. Simply speaking, plasma is a kind of ionized gas, into which sufficient energy is provided to free electrons from atoms or molecules and to allow both species, ions and electrons, to coexist. Generally, the plasma state can be divided into two main types (Fig. 1): low-temperature plasma – that is the state in which only a part of gas molecules is ionized and the gas is a mixture of electrons, ions, free radicals, excided and neutral molecules – and high-temperature plasma, in which all atoms are fully ionized. The latter type of plasma can be found, for example, in

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the Sun or in laboratories involved in nuclear fusion research, but this type of plasma is rather not interesting as a technology for the preparation of new materials.

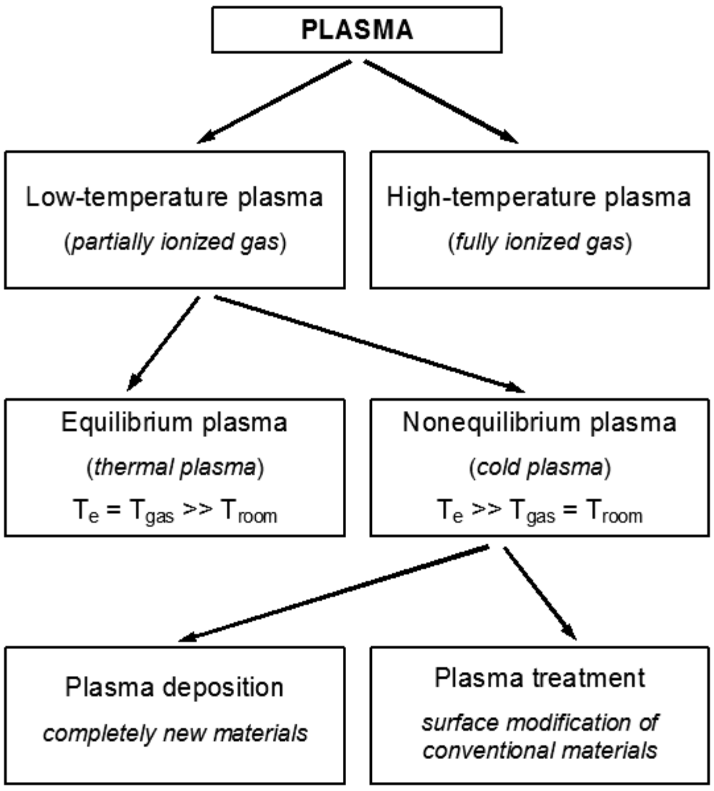

Fig. 1. Classification of the plasma types.

The low-temperature plasma can be divided, in turn, into two further types (Fig. 1): equilibrium and non-equilibrium plasmas. In the equilibrium plasma, often called the thermal plasma, electrons and the rest of plasma species have nearly the same temperature ($T_e \approx T_{gas}$), much higher than the room temperature. Such plasma is generated, for example, in plasma jets and torches. On the other hand, the non-equilibrium plasma, called sometimes the cold plasma, is characterized by the lack of thermal equilibrium between electrons and the rest of plasma species. In this case the electron temperature is in the range of 10^4–10^5 K, whereas the rest of the species are at temperature close to the room temperature. Under such conditions, chemical processes (e.g. chemical synthesis of new materials) can be performed at the room temperature using energetic electrons to cleavage covalent bonds in the gas molecules. By contrast, very high temperature of all the species in the thermal plasma considerably limits its application for the chemical syntheses and the surface modifications of thermal-degradable materials.

As one can see, among the various types of plasmas, the cold plasma is especially recognized as a promising tool on the road towards the search for new materials. The creation of such materials by the cold plasma technology can be carried out in two ways (Fig. 1). The first one is the deposition of completely new materials in the form of thin films, which is mainly accomplished by plasma polymerization processes (sometimes not quite correctly called plasma-enhanced chemical vapor deposition (PECVD)), and also, but relatively more rarely, by reactive sputtering processes. Thin-film materials with unusual chemical constitution, molecular construction and nanostructure can be obtained in this way (Gordillo-Vázquez et al., 2007; Konuma, 1992).

The second way consists in the modification of conventional materials, performed by their cold plasma treatment. Generally, such a treatment triggers three basic processes occurring mainly on the surface. It can create new functional groups by implantation of atoms present in the plasma, it can generate free radicals that then react with atmospheric oxygen and water molecules giving additional functional groups or can be used in grafting processes, and finally it can modify the microporous structure by the etching and degradation effects (Inagaki, 1996).

The cold plasma is most often generated in laboratories and industry by an electric glow discharge under low pressure using various frequencies of the applied electric field: audio frequencies (AF, mainly in the range of 10–50 kHz), radio frequencies (RF, mainly 13.56 MHz), and microwave frequencies (MW, mainly 2.45 GHz). Sometimes, a direct current (DC) discharge is also used. An example of typical parallel plate plasma reactor, one of those being used in our laboratory for deposition of thin films, is sketched in Fig. 2.

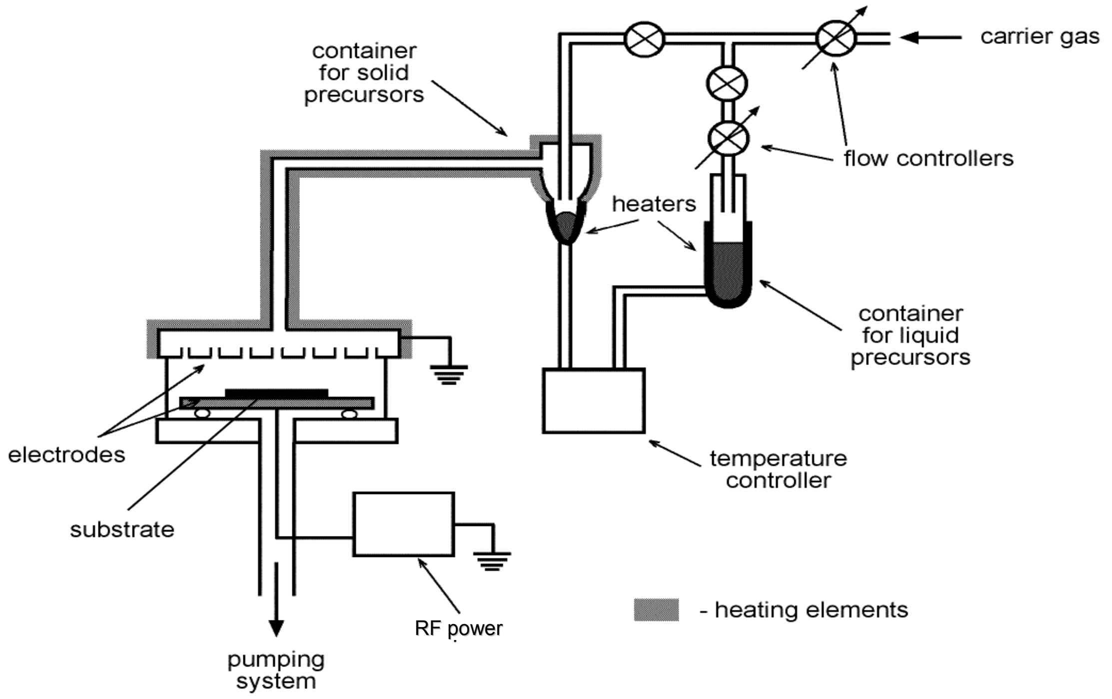

Fig. 2. A sketch of a typical parallel plate plasma reactor.

At first, the reactor chamber is evacuated down to 10^{-1}–10^{-3} Pa. Then, a precursor of plasma deposition is introduced to the chamber in the form of gas or vapor under controlled flow. Organic and inorganic gases, sublimating solids and evaporating liquids can be used as precursors. They are supplied as pure compounds or as mixtures with an inert carrier gas (e.g. argon). The carrier gas enables to generate plasma in the presence of compounds with very low vapor pressure. It is also possible to perform the plasma deposition process using a mixture of two or more precursors. Suitable selection of these compounds and their concentrations in the reactor chamber make it possible to control the molecular structure of deposited films, and consequently – properties of the films. In the reactor chamber with reactive gases, the glow discharge is generated between two internal metal electrodes by means of an appropriate generator. As a result of chemical processes proceeding in the plasma, a thin film of a new material, commonly referred to as "plasma polymer", is deposited on the electrode surfaces as well as on any substrate being in the plasma region. The same reactor can be also used for the modification of conventional materials. In this procedure, however, only "non-polymerizable" gases (e.g. Ar, O_2, N_2, NH_3) are utilized as precursors of plasma processes.

Another important plasma reactor employed in our study for the preparation of very interesting new materials is the so-called "three-electrode AF reactor". A schematic view of this reactor is shown in Fig. 3. A small electrode, on which films are deposited, is placed horizontally between two main perpendicular electrodes maintaining a glow discharge (10–50 kHz). The small electrode is coupled with the powered main electrode by a variable capacitor. The coupling capacitance controls the sheath voltage of the small electrode ($V_{(-)}$) and, in consequence, the impact energy of ions bombarding the growing film, independently of the plasma chemistry processes proceeding in the gas phase. It is especially striking that in some cases a very small variation of the bombarding ion energy in a defined range of its values is sufficient to create a drastic change in the electronic structure of deposited films (Tyczkowski, 1999). Thin films of this type will be discussed later in this Chapter (*Sec. 4.1.*).

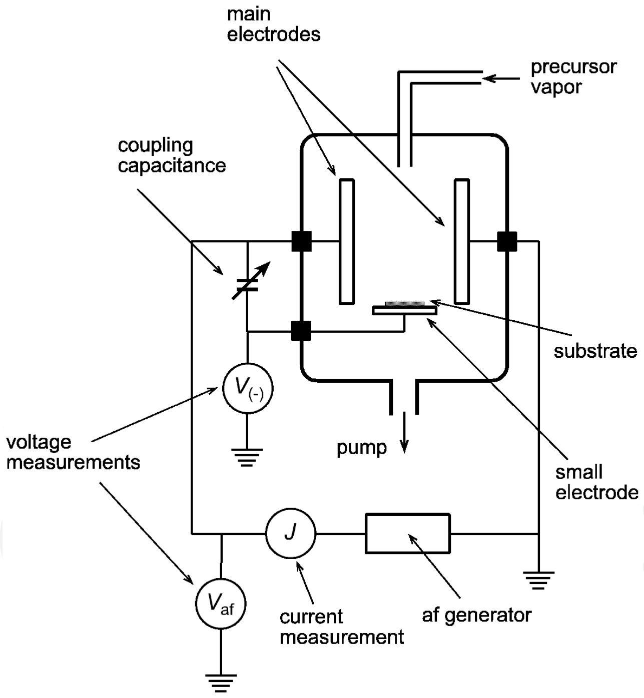

Fig. 3. A schematic diagram of the three-electrode AF reactor.

A useful variant of the fabrication of new materials by the cold plasma technique is the reactive sputtering. A schematic diagram of a typical set-up for sputtering deposition is sketched in Fig. 4. Positive ions that are produced in RF plasma generated in an inert gas, for example Ar, bombard the target surface (supplied with the negative self-bias) and cause the sputtering of its material. The sputtered material condenses on the substrate that is located out of the plasma region. If we use some reactive gas (e.g. O_2, N_2, CH_4), the target material takes part in chemical processes after sputtering and finally a new converted material is deposited. This is the so-called reactive plasma sputtering.

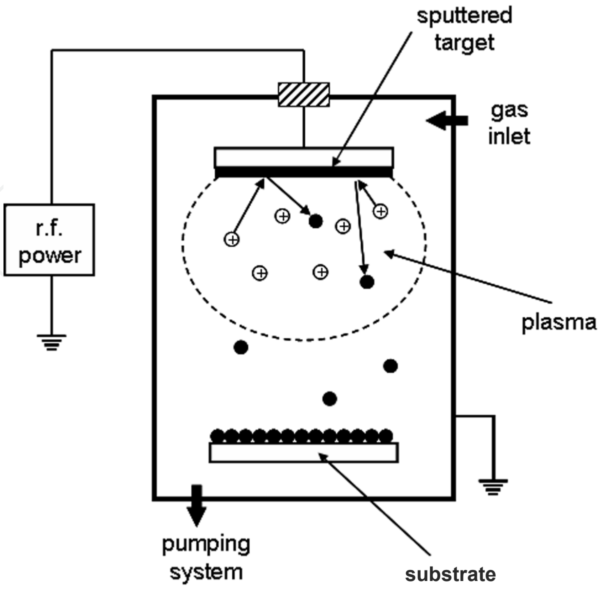

Fig. 4. A schematic diagram of a typical set-up for sputtering deposition.

For the sake of formality, it should be added that recently more and more attention has been focused on the cold plasma processes performed under atmospheric pressure conditions (Belmonte et al., 2011). However, plasma processes carried out under low pressure are, so far, still dominating in the cold plasma technology.

3. Plasma deposition of new materials

Since the first literature reports describing – nearly 140 years ago – the formation of solid products during electrical discharge in a tube filled with acetylene, many researches working in the field of plasma chemistry have observed the presence of high molecular weight materials as reaction by-products. These products were usually considered disadvantageous – they were deposited on the reactor walls and, due to their good adhesion to glass and insolubility in organic solvents, were not easily removable. They began to stimulate a scientific interest as late as in the sixties of the 20th century only, after Goodman (Goodman, 1960) had reported a successful application of plasma polymerized styrene films as an insulating layer in nuclear batteries. A vast amount of literature concerning plasma deposited films (plasma polymers), their properties, structure and mechanism of formation as well as potential application in various technologies has been published since then. The application ability of plasma polymers originates from both their often unique properties and relative simplicity of their production (Biederman, 2004; and references therein).

At the beginning, the interest was mainly limited to classical monomers, i.e. substances known to be able to polymerize in the conventional way (e.g. ethylene, styrene, butadiene). Hence, at that time the term "plasma polymer" was introduced as the result of the supposed analogy to conventional polymerized materials. In soon turned out, however, that many other low molecular weight organic, organometallic and inorganic compounds undergo plasma polymerization as well. Plasma polymers and conventional polymers, even though they should be produced from the same precursor (monomer), have practically nothing in common. The fundamental difference is that mer units cannot be defined in the case of plasma polymers. A large variety of chemical species created in the plasma, statistical combination them into high molecular structures and generally a high degree of their crosslinking cause that the structure of such a material is very often much closer to that of covalent glasses than that of conventional polymers.

Frequently plasma polymers are not classified in respect of the type of monomer but from a point of view of their chemical composition and morphology. For example, amorphous (a-) covalent material obtained by plasma polymerization of silane (SiH_4), which is composed of silicon and hydrogen, can be termed as a-Si:H. In turn, amorphous plasma polymer deposited from acrylonitrile (C_3H_3N) can be called as plasma-polymerized (pp-) acrylonitrile or a-C_XN_Y:H. It is usually met, but it is not a rule, that if the plasma polymer structure is close to a covalent glass structure, the latter notation is used. If plasma polymer reveals nano- or microcrystalline structures, prefixes nc- or μc- are put in the place of a-.

The structure and properties of plasma polymers are closely connected with a thin-film form, in which they are produced. In general, the thickness of the films is between a few nanometers and a few micrometers. Appropriate choice of precursors and plasma process parameters allow for the preparation of such thin films with a huge variety of structure and properties. Hence, there is a wide and diverse range of their current and anticipated applications, such as electronic and photoelectronic materials, insulating coatings, catalytic films, semi-permeable and electrolyte membranes, protecting layers, and many others. Some of these uses are also related to the electrochemical systems.

4. Optoelectronically active materials

Optical and electrical properties of plasma deposited films, sometimes unique indeed, as well as the easy of their deposition, at low temperature and low cost, on inexpensive substrates of almost any size and shape, render these materials very attractive for optoelectronic applications. The possibility to tailor optical parameters, such as refractive index and extinction coefficient, and what is particularly important - the ability to adjust parameters of the electronic structure, such as transport gap, optical gap, density of localized states, etc., recommend these plasma films as active photoelectric elements, e.g. for solar cells and water splitting cells.

4.1 Thin-film solar cells

Among the plasma deposited amorphous semiconductors, which have so far been studied in greatest detail and also appear to be of greatest applied interest, are hydrogenated amorphous silicon films (a-Si:H). Initial studies of this material were done in the sixties of the 20th century, when the RF glow discharge deposition of a-Si:H from silane was demonstrated. This was followed by the very important works that reported on successful *n*- and *p*-doping a-Si:H. It was really surprising, because previous attempts to dope thermally evaporated a-Si had failed. As it turned out, hydrogen was responsible for this effect. In 1975 and 1976, research confirmed that plasma-deposited films from silane contained hydrogen. Hydrogen serves primarily to passivate the dangling-bond defects and thus to decrease the density of localized states in the mid-gap.[2] Thermally evaporated a-Si has about 10^{26} eV^{-1}m^{-3} states in the mid-gap, whereas the density of states for typical a-Si:H films is about 10^{21} eV^{-1}m^{-3}, i.e. five orders of magnitude lower. This just explains why one can control the electronic properties of a-Si:H by doping with donor and acceptor centers, contrary to a-Si (LeComber & Spear, 1979).

The most frequent method used to prepare doped films is plasma copolymerization from a mixture of the film precursor and the dopant agent. Diborane (B_2H_6) and phosphine (PH_3) are often used as sources of acceptor centers (boron atoms) and donor centers (phosphorus atoms), respectively. Recently, liquid compounds instead of these gases, such as triethylboron ($B(C_2H_5)_3$) and trimethylphosphine ($P(CH_3)_3$) have become more and more popular dopant agents. They are less toxic, more stable and their low vapor pressure offers facilities for precise controlling of the doping process. In turn, as a-Si:H film precursor, one can use not only SiH_4, but also, for example, a mixture of $SiCl_4$ and H_2, disilane (Si_2H_6), trisilane (Si_3H_8), cyclohexasilane (Si_6H_{12}), etc. (Pokhodnya et al., 2009; Searle, 1998; Tyczkowski, 2004). So, as one can see, the possibilities of designing and controlling the molecular and electronic structure of plasma deposited films are indeed enormous.

As an example of designing the electronic structure of a-Si:H films, the electrical conductivity of these films doped with acceptors (boron) and donors (phosphorus) is shown in Fig. 5. The room-temperature conductivity σ of the films is plotted against the ratio of the number of dopant agent molecules to the number of silane molecules in the gaseous mixture. In the center of the graph, the conductivity around 10^{-6} S/m is representative of undoped a-Si:H films, which typically are *n*-type material. Thus, even a small quantity of P atoms (donors) increases σ rapidly. In the case of B atoms (acceptors), however, we see that initially σ decreases to about 10^{-10} S/m. This is connected with the transition from *n*-type to *p*-type material (LeComber & Spear, 1979; Tyczkowski, 2004).

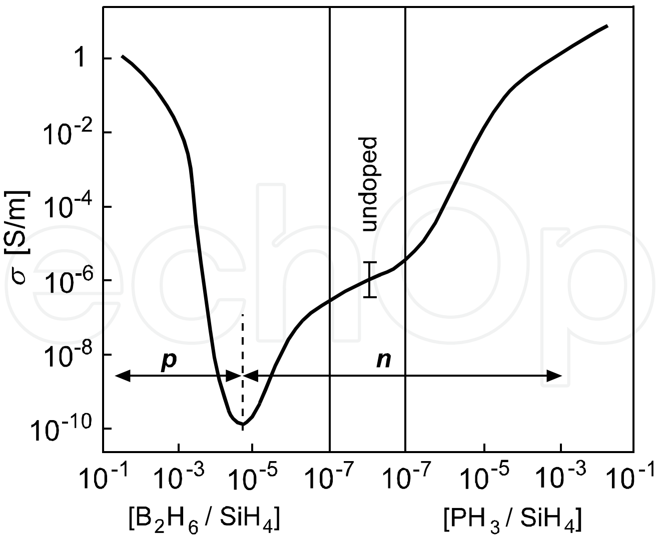

Fig. 5. Room temperature conductivity σ of *n*- and *p*-type a-Si:H, plotted as a function of the gaseous precursor ratio (Tyczkowski, 2004).

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[2] For more detailed description of the electronic structure models for plasma deposited amorphous films, see, for example, (Tyczkowski, 2004).

Thin-film solar cells are without doubt one of the most spectacular application (except thin-film transistors) of a-Si:H films obtained by plasma polymerization processes. Since the demonstration of the first a-Si:H photovoltaic devices at RCA laboratories in 1976 (Carlson & Wronski, 1976) there has been remarkable progress in the development of a-Si:H solar cells, spurred, first of all, by the wide demand for a low cost, clean and safe energy (Mueller, 2009).

The most extensively studied a-Si:H solar cells, due to their highest conversion efficiencies, are those fabricated in the form of *p-i-n* devices. Typically, the *p*-a-Si:H film is less than 10 nm, the undoped *i*-a-Si:H is between 200 and 700 nm and *n*-a-Si:H layer is approx. 30–50 nm. The layers are deposited on each other in successive plasma reactor chambers connected by vacuum locks. A metallic electrode is used as a substrate. An opposite optically transparent and electrically conducting electrode (e.g. ITO film) is deposited from the top. Today, the commercial large-area solar cell modules based on a-Si:H are fabricated with a stabilized conversion efficiency (the ratio of the maximum power output to the solar energy input) in the 4–6 % range (Green, 2007).

To improve the efficiency and stability of a-Si:H solar cells a lot of various experimental investigations coupled with theoretical device modeling and design analysis have been carried out for the past two decades. Among the most important ideas are multiple-junction solar cell structures fabricated from different amorphous semiconducting films, in addition to a-Si:H, such as a-Si_XC_Y:H, a-Si_XGe_Y:H, and other related films. These films, classified as silicon-based alloys, can be plasma deposited from single precursors, e.g. tetramethylsilane ($Si(CH_3)_4$) or mixtures of precursors such as SiH_4 and CH_4, SiH_4 and GeH_4, etc. The films can be also doped with donor or acceptor atoms introduced to their structure during the plasma deposition process by addition of an appropriate dopant agent. An example of such a multiple-junction solar cell could be a triple-junction system composed of three *p-i-n* structures plasma-deposited on top of one another, prepared consecutively with the following amorphous semiconductors: a-Si:H, a-$Si_{X1}Ge_{Y1}$:H and a-$Si_{X2}Ge_{Y2}$:H. The system gives the stable efficiency of 10.4 % for a 900 cm^2 module (Green et al., 2011).

Apart from the thin films of amorphous semiconductors, nanocrystalline form of these materials has also attracted much attention due to its higher efficiency and stability. While an amorphous semiconductor, for example, a-Si:H is a single phase material, its nanocrystalline form (nc-Si:H, also very often, but less correctly, called μc-Si:H) can be described as a bi-phasic material consisting of a dispersion of silicon nanocrystals embedded in silicon or other silicon-based hydrogenated amorphous matrices, whose volume fraction could be varied by selecting the proper plasma deposition conditions. The nc-Si:H films have been recently demonstrated to be an interesting alternative to a-Si:H films (Conibeer et al., 2006).

Although the efficiency of a-(or nc-)Si:H based solar cells is considerably lower than, for example, that for Si crystalline cells (25.0±0.5 %) or GaAs crystalline cells (26.1±0.8 %) (Green et al., 2011), much lower cost and easy of production are the major arguments in favor of the plasma-deposited solar cells. It should be noted that the last word has not been said yet in this regard and further significant progress is expected, provided that the substantial evolution in the field of new materials will be achieved.

Among the promising materials in this respect are thin films (e.g. a-Ge_XC_Y:H, a-Si_XC_Y:H, a-Sn_XC_Y:H, a-Pb_XC_Y:H), which can exist in two forms with totally different electronic structures, namely, the semiconducting (a-S) and insulating (a-I) form. In general, a typical amorphous semiconductor is characterized by localized states that form only short tiles in the mid-gap above and below the valence and conduction bands of extended states whereas in amorphous insulators all states are localized. In consequence, drastic differences in electrical and optical properties of a-S and a-I films are observed. It turned out that a particularly useful system for the production of these two qualitatively different materials is the three-electrode reactor presented in *Sec. 2*. Both a-S and a-I can be fabricated in this reactor from a single precursor (organometallic or organosemimetallic compound, e.g. tetramethylsilane, tetramethyltin, etc.) in the same deposition process, only by changing the impact energy of ions bombarding the growing film. The ion energy is controlled by the sheath voltage of the small electrode ($V_{(-)}$), which in turn is governed by the coupling capacitance (Fig. 3). It is especially striking that very small variation of the sheath voltage in a defined range of its values is sufficient to create the step change in the electronic structure of deposited film. This "transition" between two forms of the film (a-I and a-S) has been called the a-I–a-S transition. As an example, changes in electrical conductivity σ of selected films deposited in the three-electrode reactor are shown in Fig. 6 (Tyczkowski, 2004, 2006).

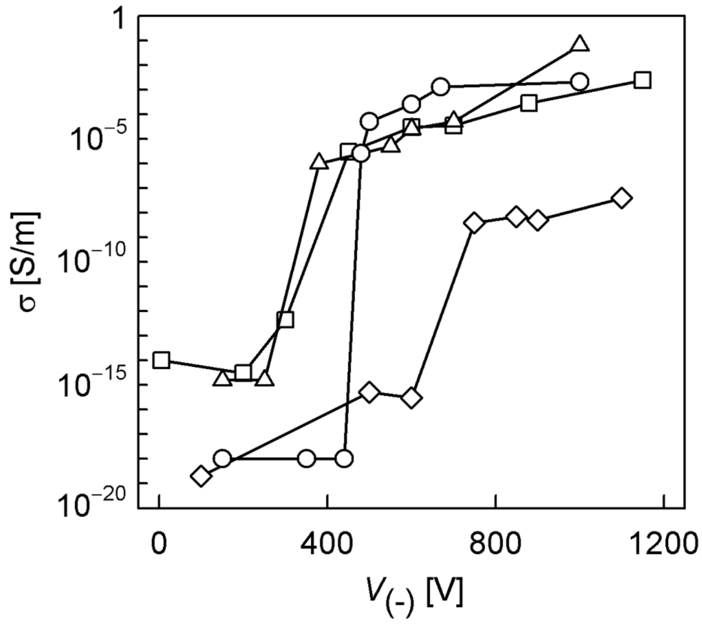

Fig. 6. Electrical conductivity σ of films deposited in the three-electrode AF reactor from organic derivatives of the carbon family as a function of $V_{(-)}$: (◇) a-Si_XC_Y:H, (○) a-Ge_XC_Y:H, (△) a-Sn_XC_Y:H, (□) a-Pb_XC_Y:H (Tyczkowski, 2006).

The existence of two qualitatively different, from the electronic structure point of view, types of plasma deposited films offers new possibilities for material technology consisting in preparation of a novel class nanocomposites formed from insulating and semiconducting fractions (in the form of clusters or layers) deposited in the same plasma process from the same single-source precursor. Without a doubt, such nanocomposites are not only interesting for solar cells, but also for other electrochemical systems. An attempt to use a-Ge_XC_Y:H films for water splitting are being undertaken now in our laboratory.

4.2 Water splitting systems

The most desirable method for production of hydrogen, which represents a sustainable fuel of the future, is photoelectrochemical (PEC) splitting of water by visible light. Theoretically, the PEC production of hydrogen has the capacity to provide global energy security at potentially low cost (James et al., 2009).

The most critical issue in 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 environment, and low processing costs. Metal oxides are most promising in this regard (Walter et al., 2010). After four decades of intensive research, however, no material has been found to simultaneously satisfy all the criteria required for widespread PEC application. No wonder that a broad search for new materials for photoelectrodes is still ongoing. Cold plasma technology is also involved in this activity (Randeniya et al., 2007; Slavcheva et al., 2007; Walsh et al., 2009; Zhu, F. et al., 2009).

A typical simple PEC cell with schematic representation of charge transfer is shown in Fig. 7. The cell is constructed from a semiconducting photoanode and metal cathode. The basic reaction steps involved in the PEC process in the cell are as follows (Nowotny et al., 2006): *1*. Photoionization over the band gap of the semiconductor:

$$h\nu \rightarrow e^- + h^+ , \tag{1}$$

where h is the Planck constant and ν is the light frequency; *2*. Charge separation:

$$e^- + h^+ \rightarrow e^-_{\mathrm{bulk}} + h^+_{\mathrm{surface}} ; \tag{2}$$

3. Reaction between water molecules and holes at the surface of the photoanode:

$$\mathrm{H_2O} + 2h^+ \rightarrow 2\mathrm{H}^+ + \tfrac{1}{2}\,\mathrm{O_2}; \tag{3}$$

4. Transport of hydrogen ions from the photoanode to the cathode through the liquid electrolyte; *5*. Transport of electrons to the cathode thorough the external circuit; and *6*. Reaction between electrons and hydrogen ions at the cathode:

$$2e^- + 2\mathrm{H}^+ \rightarrow \mathrm{H_2} . \tag{4}$$

The first PEC cell for water splitting, with a rutile TiO_2 photoanode and Pt counter cathode, was reported in 1972 (Fujishima & Honda, 1972). Following this discovery, intensive studies aiming at increasing the energy conversion efficiency of solar energy into chemical energy have been carried out, mainly on the analogous PEC cells, using TiO_2 as the photoanode. Then other oxides, e.g. Fe_2O_3 and WO_3, have been also tested. Despite the good catalytic activity of oxides such as TiO_2, they are generally limited by too large band gaps (approx. 3 eV), which fail to absorb a significant fraction of visible light, resulting in poor solar to hydrogen conversion efficiencies under terrestrial conditions. This value should be reduced to 1.7–2.0 eV. Besides, there is a range of other problems, like incorrect alignment of band edges with respect to the water redox potentials, energy losses due to charge recombination, low density of surface active sites reacting with water molecules, low corrosion resistance, etc. Thus, the majority of PEC oxide research has focused on trying to solve these problems by the modification of known photoactive oxides (through their doping or alloying), and very recently also by creation of new materials. Invaluable in this respect seems to be the cold plasma technology, which allows to design the structure of fabricated materials in a very wide range (Walsh et al., 2009).

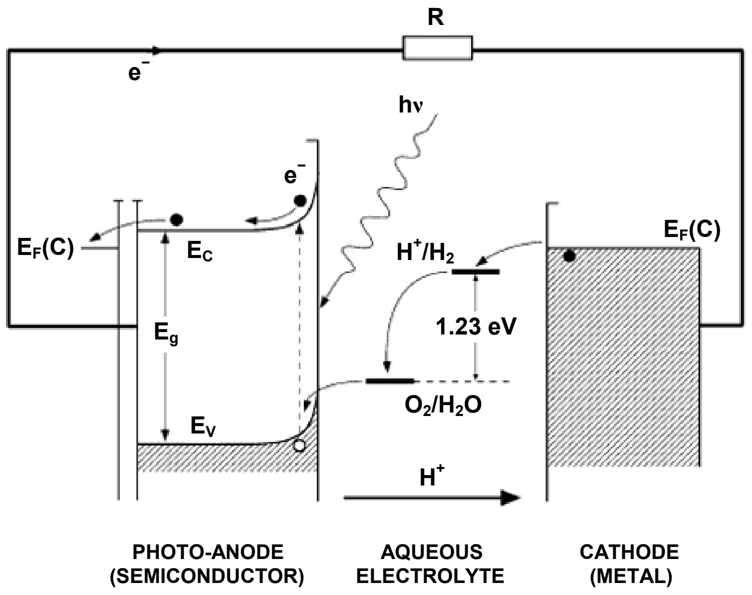

Fig. 7. Schematic representation of charge transfer within a photoelectrochemical cell involving a semiconducting photoanode and metal cathode (Nowotny et al., 2006).

The most attractive oxide to date, namely TiO_2, has already been repeatedly produced by the cold plasma technology. In most reported works, either $TiCl_4$ or Ti alkoxides (mainly titanium tetraisopropoxide, $Ti(OC_3H_7)_4$) are used as the Ti-containing precursors of the plasma polymerization (PECVD) process, resulting in amorphous or crystalline films, with the nonstoichiometric (TiO_X) or stoichiometric (TiO_2) structure. For all of these films, their physicochemical properties are strongly dependent on the film structure, which can be effectively controlled by the deposition conditions (Battiston et al., 2000; Borrás et al., 2009; daCruz et al., 2000; Maeda & Watanabe, 2005; Nakamura et al., 2001).

TiO_2 films are also obtained in a wide range by the reactive sputtering, usually using pure titanium as a target, and O_2 as reactive gas. Similarly, as in the PECVD technique, also in this case, the sputtering process conditions control the structure of the deposited films, which in turn affects to a large extend the optical and photoelectrochemical properties of the films (Brudnik et al., 2007; Dang et al., 2011; Huang et al., 2011).

A particularly useful feature of the cold plasma technology is the possibility of co-deposition either by copolymerization of a mixture of precursors or by co-sputtering using more than one target or a mixture of several reactive gases. In this way we can get doped films as well as films with alloy-type structures. Numerous studies have been already done on the introduction into the TiO_2 structure other atoms (e.g. C, N, S). For example, PECVD with the DC discharge carried out using mixtures of $Ti(OC_3H_7)_4$ and nitrogen led to a Ti(OCN) film structure (Randeniya et al., 2007; Wierzchoń et al., 1993). Instead of nitrogen, ammonia can be introduced to plasma reactors (Weber et al., 1995). Precursors containing nitrogen in their chemical structure, e.g. tetrakis(dimethylamido) or (diethylamido)-titanium ($Ti(N(CH_3)_2)_4$ or

$Ti(N(C_2H_5)_2)_4$) were also utilized (Raaijmakers, 1994). By properly adjusting the composition of the reaction mixture and the conditions of the plasma, a film structure similar to stoichiometric TiN can be obtained (Weber et al., 1995). In turn, the films composed mainly of titanium and carbon (TiC_X) were fabricated leading PECVD process in a mixture of $TiCl_4$ and hydrocarbons (Täschner et al., 1991). TiO_2 films with N and C atoms were also obtained by reactive sputtering of titanium in an appropriate gas mixture. This method also proved to be useful for the production of nanocomposite thin films for photoanodes, e.g. Au:TiO_2 films sputtered (using an RF discharge) from Ti and Au targets in O_2 as the reactive gas (Naseri et al., 2011).

The cold plasma deposition method has been used to produce, in addition to films based on TiO_2, other films that constitute an interesting material for the photoelectrodes. For example, iridium oxide (IrO_2) (Slavcheva et al., 2007), tantalum nitride (Ta_3N_5) (Yokoyama et al., 2011), ruthenium sulfide (RuS_2) (Licht et al., 2002), and tungsten trioxide (WO_3) (Garg et al., 2005) films were prepared by reactive sputtering. WO_3 was also deposited by PECVD technique, feeding the RF plasma reactor with a gas mixture of tungsten hexafluoride (WF_6) and oxygen (Garg et al., 2005).

Recently, a proposal to employ a-Si_XC_Y:H films as photoelectrodes for PEC cells has been presented (Zhu, F. et al., 2009). The films were fabricated by PECVD using a SiH_4, H_2 and CH_4 gas mixture. It was found that the a-Si_XC_Y:H photoelectrode behaves as a photocathode, where the photo-generated electrons are injected into the electrolyte and reduce H^+ ions for hydrogen evolution. The use of this photoelectrode led to a solar-to-hydrogen conversion efficiency higher than 10%. It should be noted that a-Si_XC_Y:H films deposited by PECVD technique have been extensively investigated for a long time. A lot of gas mixtures (e.g. SiH_4 and hydrocarbons) or single compounds (e.g. tetramethylsilane ($Si(CH_3)_4$)) are used as precursors of the deposition process. In some cases, dopant agents are also added. In fact, the films can be accurately produced according to the designed electronic structure and photoelectronic properties, which can change over a very wide range. For instance, their electrical conductivity changes from 10^{-18} to 0.1 S/m and the optical gap shifts between 1.8 and 3.2 eV (Tyczkowski, 2004).

In the past five years, cobalt has emerged as the most versatile non-noble metal for the development of synthetic H_2- and O_2-evolving catalysts. Among the various structures containing cobalt atoms, cobalt oxides appear to be particularly promising materials. The possibility of using such oxides to catalyze water oxidation in neutral aqueous solutions has recently experienced a burst of interest (Artero et al., 2011). There have been many reports in the literature concerning the use of cobalt oxides, mainly Co_3O_4, as electrode coatings that catalyze water oxidation. Many different methods have been applied to prepare these coatings, among others, also the cold plasma deposition technique – both PECVD and reactive sputtering. In PECVD, cobalt oxide films were obtained from volatile precursors such as bis(acetylacetonate)cobalt(II) (Fujii et al., 1995), bis(2,2,6,6-tetramethylheptan-3,5-dionato)cobalt(II) (Barreca et al., 2011), bis(cyklopentadienyl)cobalt(II) (Donders et al., 2011) or cyclopentadienyl(dicarbonyl)cobalt(I) (Tyczkowski et al., 2007). Other volatile cobalt complexes (e.g. amidinates and cyclodexrtins) are now also proposed as the precursors (Li et al., 2008; Papadopoulos et al., 2010). The sputtering process, in turn, was conducted in the presence of pure Co or Co_3O_4 as targets and plasma generated in a gas mixture containing O_2 (Ingler Jr et al., 2006; Schumacher et al., 1990). The reactive sputtering technique was also used to produce ternary cobalt spinel oxides of the type CoX_2O_4 (X = Al, Ga, In), taking the targets from Co_3O_4 and Al, Ga_2O_3 or In_2O_3. Preliminary research showed that although these materials combine excellent stability in solution and good visible light absorption properties, their performance as photoelectrochemical catalysts for water splitting is limited by the poor electrical transport properties. It is hoped, however, that the broad capabilities of plasma technology will help overcome this problem (Walsh et al., 2009).

Particularly significant is the finding that nanoclusters of Co_3O_4 are much more efficient in the PEC process than larger objects (e.g. micrometer-sized particles) of this oxide. Thus, it is very important to develop methods for producing cobalt oxides films containing Co_3O_4 nanoclusters. Recently, mesoporous silica has been used as a scaffold for growing Co_3O_4 nanocrystals within its naturally parallel nanoscale channels via a wet impregnation technique. It has been found that rod-shaped crystals measuring 8 nm in diameter and 50 nm in length are interconnected by short bridges to form bundled clusters. The bundles are shaped like a sphere with a diameter of 35 nm (Jiao & Frei, 2009). This report aroused great scientific interest. However, it should be noted that films composed of nanoclusters can be easily deposited on a flat surface without any special mesoporous structure, only involving the plasma deposition technique for this purpose. Using this method, nanocrystalline films of cobalt oxides have been already obtained. For example, small particles of CoO_X in the range of 2–10 nm in diameter were deposited in this way on TiO_2 support (Dittmar et al., 2004). If CoO_X films were fabricated on a substrate at elevated temperature (150–400°C), then columnar grains with average diameter size at the film surface of 35–60 nm were formed (Fujii et al., 1995). Research conducted recently in our laboratory has led to the cobalt oxide films containing 4–8 nm sized Co_3O_4 crystals, whose size can be controlled by the plasma deposition process (Tyczkowski, 2011; Tyczkowski et al., 2007). These films will be discussed in more detail in *Sec. 5.1*. It should be noted, however, that we are also now starting work on their application to the water splitting.

Although research on water splitting, conducted using the cold plasma technology to produce thin-film coatings on photoelectrodes, is only beginning, the obtained results give cause for great hope. Plasma deposited films by both PECVD and reactive sputtering can reveal very high incident photon conversion efficiency (Randeniya et al., 2007). These films also appear to be better as photoelectrodes than the corresponding materials produced by other method (Naseri et al., 2011).

The PEC process can be realized not only in cells with two electrodes separated from each other, which was discussed above, but also when the electrodes are in direct close contact. Much attention in this regard has been paid for systems where both electrodes are located within a single grain. Such a structure may be considered as a microsized PEC cell. The best analogue of the PEC cell shown in Fig. 7 is a microsized cell formed of a small semiconductor grain (e.g. TiO_2) and noble metal islets (e.g. Pt) deposited on its surface. Then, the surface of the semiconductor grain and the metal act as photoelectrode and counter electrode, respectively. More sophisticated systems with a bifunctional catalyst have been also proposed. In this case, anodic and cathodic photoactive islets (several nm in size) are deposited onto the same semiconducting nanoparticle (tens of nanometers in size) (James et al., 2009). These microsized PEC cells produce, however, a mixture of oxygen and hydrogen. To receive these gases separately, reactors composed of two chambers connected by a diffusion bridge are used. In one chamber there is a suspension of nanoparticles only with an anodic catalyst while in the second one – only with a cathodic catalyst (James et al., 2009).

In the field of microsized PEC cells, the plasma techniques have also proved to be very useful, both in the synthesis of semiconducting particles and in the deposition of active catalysts of them. For the production of powders, in a very wide range of grain sizes (from single nanometers to tens of micrometers) mainly the thermal plasma (see: Fig. 1) is utilized (Ctibor & Hrabovský, 2010; Karthikeyan et al., 1997). The PECVD technique is, however, also engaged for this purpose. By this technique, TiO_2 nanocrystalline powder was prepared, using an AF glow discharge (40 kHz) and titanium tetraisopropoxide ($Ti(OC_3H_7)_4$) with oxygen as a reactive mixture. The obtained nanocrystalline particles, with mean size of about 25–55 nm, revealed good photocatalytic activity (Ayllón et al., 1999). Another example is the synthesis of carbon-supported ultrafine metal particles by MW plasma from metal carbonyls (e.g. $Fe(CO)_5$, $Co_2(CO)_8$, $Mo(CO)_6$) as precursors (Brenner et al., 1997). In turn, noncrystalline organosilicon powder was produced by plasma polymerization of tetramethylsilane ($Si(CH_3)_4$). The ratio of elements (Si/C) as well as the chemical structure of the grains was highly dependent on the plasma process conditions (Fonseca et al., 1993).

As already mentioned earlier, an important feature of the PECVD method is the possibility of copolymerization. This route was used to prepare TiO_2 nanoparticles doped with Sn^{4+} ions. The plasma process was performed in a mixture of $TiCl_4$ and $SnCl_4$ with an appropriate molar ratio. It was found that photocatalytic activity of TiO_2–Sn^{4+} nanoparticles was much higher than those of the pure TiO_2 (Cao et al., 2004). Wide possibilities of the plasma technique also allow to produce nanoparticles of doped semiconducting organic polymers, e.g. polypyrrole plasma doped with iodine (Cruz et al., 2010). This is only a matter of time when such organic nanoparticles with anchored a molecular water oxidation catalyst will be produced by plasma polymerization.

The deposition of catalytically active coatings onto the surface of already prepared particles has also been performed. In this case, however, to achieve efficient coating of the nanoparticles, a special construction of the plasma reactor chamber is needed, for example, with 360° continuous rotation. In such a reactor, TiO_2 nanoparticles were coated with thin film produced by plasma polymerization of tetramethyltin ($Sn(CH_3)_4$). Subsequently, the coated particles were heated in air to remove the carbonaceous material while, simultaneously, oxidizing tin atoms to tin oxide. To obtain partially fluorinated tin oxide, hexafluoropropylene oxide (C_3F_6O) was added to $Sn(CH_3)_4$. It should be noted that significantly increased photocatalytic activity of TiO_2 nanoparticles was achieved using the PECVD approach (Cho, J. et al., 2006).

Finally, one more type of water splitting cells should be mentioned, namely integrated photovoltaic–electrolysis (PV-PEC) cells. In this type of devices, the photovoltaic cell and the electrolyser are combined into a single system, in which the light-harvesting solar cell is one of the electrodes. Very often, thin-film solar cells fabricated by the cold plasma deposition method are employed in the PV-PEC devices (Kelly & Gibson, 2006). A diagram of such a system with a simply a-Si:H solar cell is shown in Fig. 8. There is no doubt that the role played by the cold plasma deposition technique in the creation of such systems is unquestionable (see: *Sec. 4.1.*).

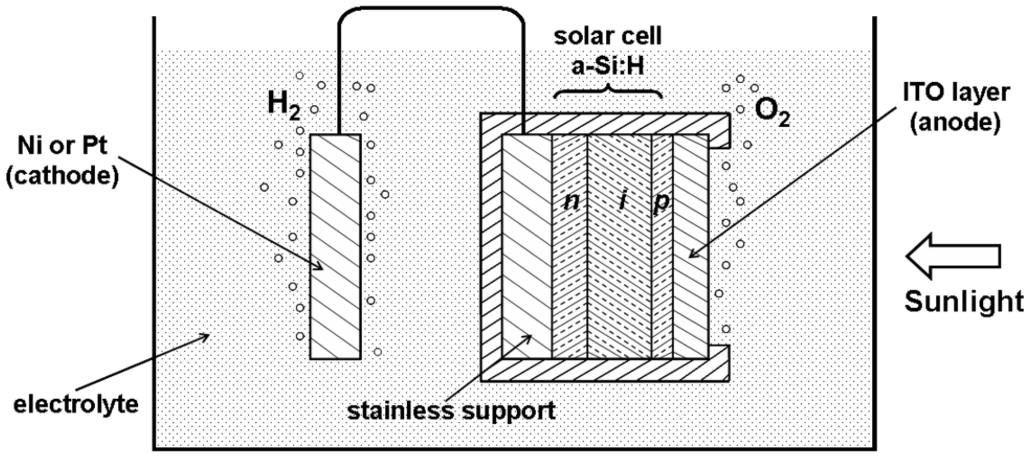

Fig. 8. Schematic representation of a photovoltaic–electrolysis system based on a simply a-Si:H solar cell (Kelly & Gibson, 2006).

5. New types of electrodes for electrochemical cells

The potential applications of plasma polymers as materials for electrochemistry are primarily associated with the possibility of designing their electronic structure and thereby with the designing of their electrical properties. Plasma deposition from diverse precursors and their mixtures, performed under various conditions of the process, leads to a huge variety of thin films characterized by a broad spectrum of electrical properties. In Fig. 9 a diagram of the conductivity typical for different plasma polymer types is presented. As one can see, the whole range from 10^{-18} S/m to 10^{6} S/m is covered by plasma deposited films. Insulating, semiconducting (of different types of conductivity) and metallic films can be obtained in this way (Tyczkowski, 2004). Some of these films can reveal a significant activity in electrochemical processes. Photocatalytic activity of such films was already discussed in the previous section (*Sec. 4.2.*).

Taking into account the electrical properties mentioned above as well as another important feature of plasma polymers, namely the membrane nature, which is very often revealed by these films, a new fascinating electrocatalyst structure has been proposed. An effective electrocatalyst must satisfy many requirements, such as high activity, high electrical conductivity, and long-term stability, which may be in conflict with each other. One possible way to solve these conflicts is the use of composite materials, where the matrix and the dispersed phase are independently selected. A successful approach is that of associating a highly conducting (though catalytically inert) matrix with an active (though less conducting) dispersed phase. When the matrix is permeable, one has a three-dimensional (3D) catalyst: all catalytic particles are active, irrespective of their position in the composite. Fig. 10 schematically represents the operation of such a system.

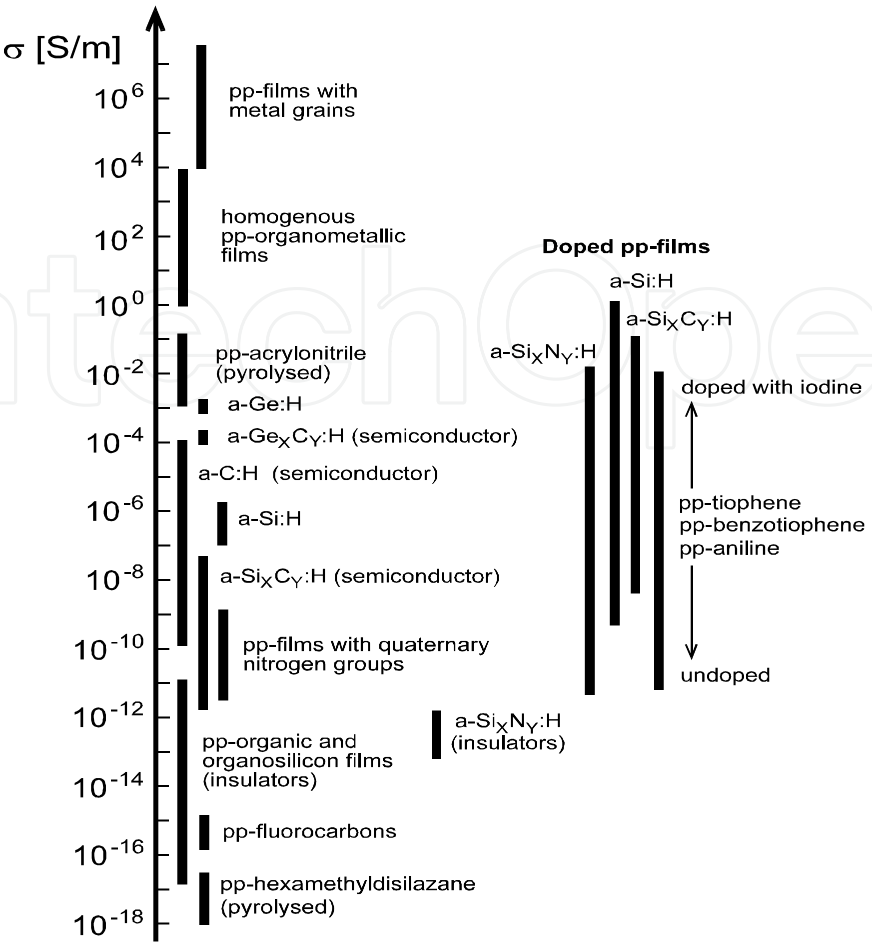

Fig. 9. Room-temperature conductivity *σ* of the main groups of plasma polymers (Tyczkowski, 2004).

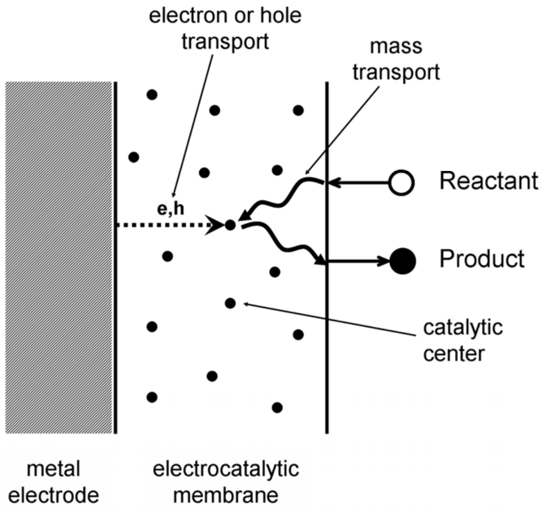

Fig. 10. Model of a three-dimensional (3D) electrocatalytic membrane (Tyczkowski, 2010).

One of the first 3D-electrocatalyst electrodes was tested for the reduction of molecular oxygen. The electrode was made of a conducting matrix, formed by plasma polymerization of acrylonitrile, and cobalt atoms playing the role of active centers, which were introduced to the matrix during the deposition process from bis(acetylacetonate)cobalt(II) precursor (Doblhofer & Dürr, 1980). Just this one example shows how the great possibilities for the construction of electrochemical electrodes are inherent in the plasma deposition technique.

5.1 Catalytic electrodes for fuel cells

Fuel cells are electrochemical membrane reactors that are able to convert chemical energy from a fuel directly to electrical energy through a chemical reaction with oxygen. Hydrogen is the most common fuel, but alcohols like methanol and hydrocarbons such as CH_4 are also used. Although there are many types of fuel cells, all of them consist of two electrodes (negative anode and positive cathode) and an electrolyte (liquid or solid) that allows ionic charges to move between the electrodes. Recently, a lot of effort has gone into improving the quality, reliability, and efficiency of these components by their modification and introduction of new materials (Carrette et al., 2000; Sundmacher, 2010). The cold plasma technology is also widely involved in this process.

For more than a decade, the polymer electrolyte (membrane) fuel cells (PEFC), which can be fed with hydrogen (when proton-exchange membranes are used, such fuel cells are called PEMFC) or, for example, fed directly with methanol (direct methanol fuel cells (DMFC)), are one of the most extensively investigated types of fuel cell worldwide. This results from their high energy-conversion efficiency, relatively low operating temperature, and high power density. The basic catalytic reactions taking place at the electrodes of PEMFC are as follows (Carrette et al., 2000):

$$\text{anode} \qquad H_2 \rightarrow 2H^+ + 2e^- \tag{5}$$

$$\text{cathode} \qquad {}^1/_2\,O_2 + 2H^+ + 2e^- \rightarrow H_2O \tag{6}$$

The anode reaction consists of hydrogen oxidation to protons (hydrogen oxidation reaction – HOR). The protons migrate through the membrane to the cathode. At the cathode, oxygen is reduced (oxygen reduction reaction – ORR) and then recombines with the protons to form water. The electrodes have to be porous to gas diffusion to ensure the supply of the reactant gases to the active zones, where a catalytic material is in contact with the ionic (membrane) and electronic (catalyst substrate) conductors. Similar reactions occur at the electrodes of DMFC (for a proton-exchange membrane) (Carrette et al., 2000):

$$\text{anode} \qquad CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \tag{7}$$

$$\text{cathode} \qquad {}^3/_2\,O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \tag{8}$$

Platinum-based materials (Pt or Pt alloys) are by far the best catalysts for the hydrogen and methanol oxidation (Eqs. (5) and (7)) as well as oxygen reduction reactions (Eqs. (6) and (8)). Unfortunately, Pt is a precious, very expensive metal, which limits the widespread commercialization of Pt-based fuel cells. Besides, the stability of Pt and Pt alloys becomes a serious problem for long-term operation of the cells. Hence, extensive research is underway to overcome these difficulties. The works are going in two directions. Firstly, the new methods to ensure consumption of smaller amounts of platinum and at the same time providing a more stable and effective catalyst are developed. And secondly, the new alternative catalysts that are cheaper than platinum and exhibit at least a comparable catalytic activity are sought (Sundmacher, 2010; Wang, 2005).

As far as the methods of reducing the amount of platinum catalyst are concerned, the most promising appears to be the plasma sputtering technique. By this method, the catalytic electrodes can be prepared with a platinum loading down to 0.005 mg_{Pt}/cm^2, that is drastically lower than that for conventional Pt electrodes (0.5–1.0 mg_{Pt}/cm^2), with no detrimental effect on fuel cell performance. The Pt catalyst is dispersed as nano-clusters of controlled size (sometimes, until less than 2 nm) and controlled crystalline structure that determines the concentration of catalytically active centers. It should be emphasized that such a possibility, in principle, is given only by the application of cold plasma (Caillard et al., 2005; Caillard et al., 2009; Saha et al., 2006; Xinyao et al., 2010). As it was already mentioned, this technology also allows to put the deposited material on virtually any substrate. Thus, the Pt catalyst can be sputtered on both a porous carbon substrate forming the electrode and the surface of a polymer electrolyte (e.g. Nafion), to which the carbon electrode is then pressed.

The main requirement of a good electrode is a three-phase boundary between the fuel supply, the catalyst particle and the ionic (polymer) electrolyte. The catalyst particles also must be in direct contact with the electron conducting electrode (Carrette et al., 2000). To ensure such a contact and at the same time maximize the interphase boundary, co-sputtering or co-deposition of carbon-based material and platinum was used. Materials classified as 3D-electrocatalysts can be obtained in this way. For example, a simultaneous co-sputtering of carbon and platinum on a conventional carbon porous substrate led to high electrodes efficiency for both the hydrogen oxidation and oxygen reduction reactions. The PEMFC tested in this case achieved a specific power of 20 kW per 1 g of platinum, which is one of the best results reported so far (Cavarroc et al., 2009). Carbon and platinum can be also deposited by subsequent sputtering processes. First a porous columnar carbon film (column diameter of 20 nm) is deposited, and then these nanocolumns are decorated by Pt nanoclusters (Rabat & Brault, 2008).

Recently, interesting results have been obtained in this field by combining the plasma polymerization and sputtering methods. For instance, the synthesis of composite thin films made of platinum nanoclusters (3–7 nm) embedded in a porous hydrocarbon matrix was carried out by simultaneous PECVD of pp-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%) (Dilonardo et al., 2011). Aniline mixed with functionalized platinum nanoparticles as a precursor of PECVD was, in turn, used to prepare a typical 3D-catalyst. The plasma deposition was performed under atmospheric pressure conditions. Plasma polymerized aniline (pp-aniline), which is characterized by both electronic and ionic conductivity, associated with the Pt catalyst in a 3D porous network, without doubt lead to the development of the three-phase boundary (Michel et al., 2010).

Another idea is to deposit on the electrode surface carbon nanofibers (nanotubes) by PECVD and then decorating them by sputtered platinum nanoclusters. Generally, three consecutive plasma deposition steps are carried out to this end: the sputtering of a catalyst used to initiate the growth of the carbon nanofibers (e.g. Fe, Ni, Co), the creation of the nanofibers by PECVD from a mixture of precursors (e.g. CH_4/H_2, CH_4/N_2) and the sputtering of platinum. The plasma produced systems consisting of carbon nanofibers with a diameter of nanometers (13–80 nm) and a length of micrometers (2–20 μm) decorated with 2–5 nm Pt nanoclusters were already the object of research. It was found that such systems prepared on the electrode substrate (carbon cloth or carbon paper) significantly improve the performance of both PEMFC and DMFC compared with the conventional electrodes (Soin et al., 2010). By the way, it should be added that vertically aligned carbon nanotubes as well as graphene layers fabricated by PECVD have recently attracted research interest as supercapacitor electrode materials (Amade et al., 2011; Zhao et al., 2009).

In addition to extensive research into the production of platinum catalysts by the sputtering method, it was also trying to get them through the plasma polymerization method (PECVD). A platinum-containing organic complex, bis(acetylacetonate)platinum(II) (Pt(acac)$_2$), which is characterized by a relatively low sublimation temperature (160–170°C), was used as a precursor of 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 (Dhar et al., 2005a). The same procedure was used to prepare a composite consisting of ZrO_2 support and Pt catalyst. The support and the catalyst were deposited on a metallic substrate by 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 (Dhar et al., 2005b).

Other potential path of development of fuel cells, in addition to improving the properties of platinum electrodes, is searching for new catalytic materials. This research is mainly focused on the cathode materials, at which the oxygen reduction reactions (ORR) (Eqs. (6) and (8)) constituting the bottleneck in the fuel cell operation proceed (Wang, 2005). The cold plasma technology creates potential and real opportunities in this regard (Brault, 2011). Like the platinum catalyst, also in this case the plasma sputtering technique was used. For example, CoS_2-based thin films were prepared by this method. Electrochemical assessment indicated that the films had significant ORR catalytic activity (Zhu, L. et al., 2008). Similarly, a high ORR catalytic activity showed niobium oxinitride (Nb-O-N) films prepared by plasma (RF) reactive sputtering from a Nb metal plate under various partial pressures of N_2 and O_2 (Ohnishi et al., 2010).

Taking into account the promising electrocatalytic activity for ORR demonstrated by nanoparticles of cobalt oxides (Manzoli & Boccuzzi, 2005), we have undertaken in our laboratory an attempt to produce such a material for the PEMFC electrodes by the plasma polymerization method. The films containing CoO_X were deposited in a parallel plate RF (13.56 MHz) reactor shown in Fig. 2. Cyclopentadienyl(dicarbonyl)cobalt(I) (CpCo(CO)$_2$) was used as a precursor. As a result of the plasma deposition process, very thin films (25–750 nm) composed of a hydrocarbon matrix and amorphous CoO_X were obtained. The amorphousity was determined by the electron diffraction pattern. However, only a moderate thermal treatment was enough to transform the amorphous films into films with nanocrystalline structure of cobalt spinel (Co_3O_4) (Fig. 11). The creation of cobalt spinel nanocrystals was supported by Raman spectroscopy measurements. The electron diffraction and Raman spectroscopy measurements also allowed us to determine the nanocrystals size. It was found that this size can be controlled by parameters of the plasma deposition process. As an example, Fig. 12 shows a dependence of the average size of Co_3O_4 nanocrystals on the flow rate of CpCo(CO)$_2$ vapor through the plasma reactor. This simple example is just enough to show that the cold plasma is a very useful technique, not only for the fabrication of new materials, but also for the precise control of their structure. In the same way as the films with CoO_X, films containing CuO_X were deposited using bis(acetylacetonate)copper(II) ($Cu(acac)_2$). After feeding the reactor by a mixture of $CpCo(CO)_2$ and $Cu(acac)_2$ vapors, thin films of Co–Cu mixed oxides were also fabricated (Tyczkowski, 2011; Tyczkowski et al., 2007).

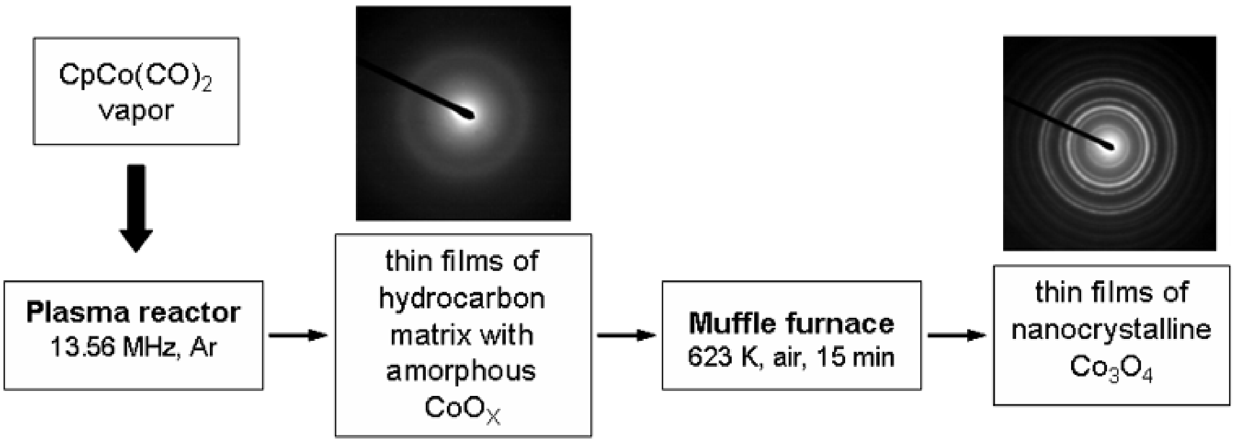

Fig. 11. Outline of the preparation process of nanocrystalline Co_3O_4 films by plasma deposition.

To test the electrocatalytic activity of the above-mentioned films, electrodes for PEMFC were prepared by the deposition of these films on a carbon paper substrate. Then the samples were thermally treated forming anode materials. The opposite electrode (cathode) was prepared from the same carbon paper covered with 10% Platinum on Vulcan XC-72 catalyst (1.56 mg/cm^2) (Kazimierski et al., 2010; Kazimierski et al., 2011). In Fig. 13, preliminary results concerning the current–voltage dependence for the tested fuel cell with various types of anode catalytic materials are shown. Although the characteristics obtained for plasma deposited materials are still far from the model system, in which both electrodes are prepared from Pt (curve f), nevertheless these results are very promising. It is enough to notice that the concentration of catalytic active centers increases with the increase of the deposition time, which is reflected in the improvement of the fuel cell characteristic (curves b, d and e). A simple calculation showed that after 80 min deposition of CoO_X, the whole deposited material loading is only 0.1 mg/cm^2 (moreover, this value is drastically reduced by the annealing) (Kazimierski et al., 2011). However, it seems to be possible to significantly increase the concentration of the centers by optimizing the plasma deposition parameters. Equally important as the centers concentration is the structure of the oxide material. One can see in Fig. 13 that the film composed of Co_3O_4 and CuO_X reveals much higher activity (curve c) than each of these oxides separately (curves a and b). Thus, it is no wonder that further intensive works in this field are planned.

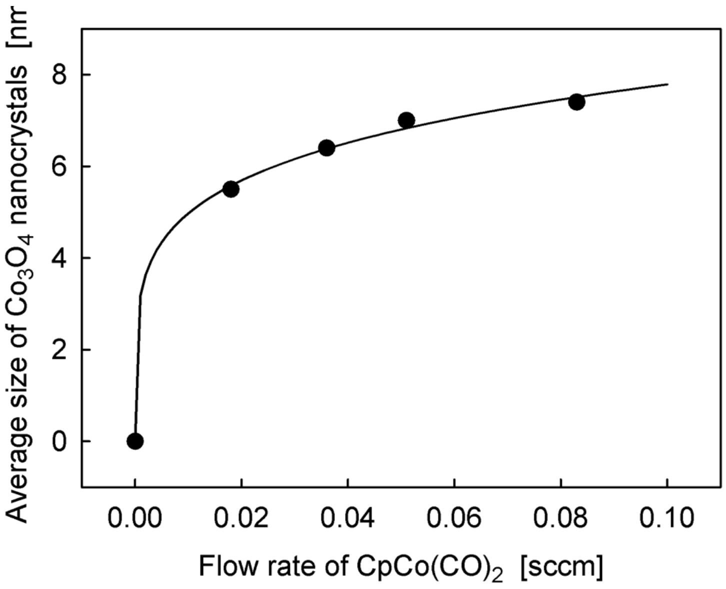

Fig. 12. Dependence of the average size of Co_3O_4 nanocrystals on the flow rate of $CpCo(CO)_2$ vapor through the plasma reactor (Tyczkowski, 2011).

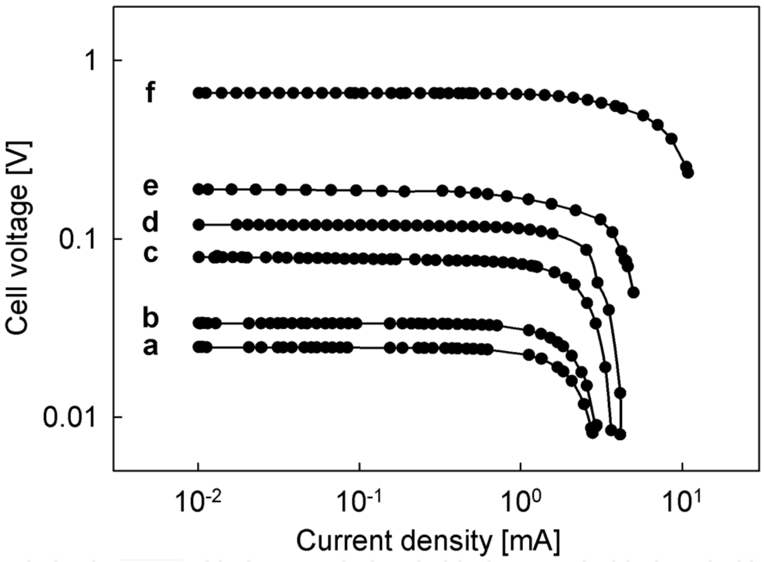

Fig. 13. Fuel cell characteristic for various cathode catalytic materials: (a) – CuO_X (*t* = 12 min); (b) – Co_3O_4 (*t* = 12 min); (c) – Co_3O_4+CuO_X (*t* = 12 min); (d) – Co_3O_4 (*t* = 60 min); (e) – Co_3O_4 (*t* = 80 min); (f) – Pt (Tyczkowski, 2011).

5.2 Electrodes for lithium-ion batteries

There has been a significant research work done in the recent past in the development of lithium-ion batteries, which are extensively applied in various electric and portable electronic devices. Although a lot of attractive cathode and anode materials for these batteries are already known, it is still lay much stress on finding new solutions in this area. Increasingly, the cold plasma technology is also used to this end. The first attempts were made in the eighties of the 20th century in Sanyo Electric Co. in Japan, where AF plasma (6.5

kHz) polymerized pyrrole as a conducting cathode layer was use for a Li-ion battery. The pp-pyrrole was deposited on one side of a porous polypropylene separator sheet, a Li layer was vapor deposited on the other site of the sheet, and stainless steel collector layers were formed on both sides by spattering. This battery showed very good properties. Research on the use of polypyrrole (also produced by plasma polymerization) for cathodes of Li-ion batteries is currently being pursued (Cho, S.H. et al., 2007). Another interesting conductive polymer, which was used as the cathode material, is plasma polymerized carbon disulfide (pp-CS_2). These films (approx. 0.5–1 μm) deposited on Pt foil showed satisfactory electrochemical activity in cells vs. Li/Li+. Compared to poly(carbon disulfide) prepared by conventional chemical means, cells having the pp-CS_2 improved cycle life because the plasma polymerized material is more crosslinked and does not depolymerize as readily (Sadhir & Schoch, 1996).

A lot of attention is also paid to entirely new anode materials. Although carbon in nowadays is used as the commercial anode material, it has several shortcomings such as, for instance, low reversible capacity that is usually ranged in 250–300 mAh/g. In order to increase this parameter, silicon with the highest theoretical capacity (e.g., 4000 mAh/g) has been proposed as a new negative electrode material. Unfortunately, this material has also serious drawbacks, which are related to the poor electrical conductivity and drastic volume changes during electrochemical reactions. To solve these problems, silicon and silicide powders with conducting materials such as metals, oxides, and nitrides are used as the composite anodes. The potential of plasma technology for the fabrication of both powders and composite systems are particularly useful in this case. For example, a complex procedure of plasma deposition was used to produce an anode material in the form of copper silicide-coated graphite particles. The graphite particles with mean diameter of 6.0 μm were covered with a very thin film of a-Si:H (30–50 nm) in the PECVD process from SiH_4. Then, copper layer was deposited on the surface of silicon-coated graphite using the next plasma technique, namely RF sputtering. After annealing at a temperature of 300°C, copper silicide was formed. This material used as the anode in Li-ion batteries revealed high capacity properties and good electrical performance (Kim, I.C. et al., 2006).

An example of particles formed by plasma methods for use in the anodes can be the synthesis of monodisperse and non-agglomerated SiO_X nanoparticles by the PECVD method from a mixture of SiH_4 and O_2 in a plasma reactor specially designed for this purpose. It should be emphasized that in this case the nanoparticle size can be controlled by the flow rate of the reactant gases through the reactor. The SiO_X nanoparticles mixed with graphite particles constitutes the anode material (Kim, K. et al., 2010).

More sophisticated materials for Li-ion electrodes were also fabricated by the cold plasma technology. Reactive co-sputtering of Sn and Ru in oxygen plasma has allowed to obtain SnO_2–RuO_2 composite thin films, which reveal unique electrochemical properties (Choi et al., 2004). As the anode, cobalt oxide thin films deposited by reactive sputtering of Co in O_2 plasma were also tested with success. It was found that these films contained Co_3O_4 grains with the size of 4–25 nm (Liao et al., 2006).

6. Other components of electrochemical cells

Plasma deposited thin films are not only very useful for creating electrochemical cell elements where they must be characterized by high electrical conductivity (optoelectronically active materials, electrode materials), but also there, where this conductivity should be as low as possible. Plasma polymers with very low electrical conductivity (see: Fig. 9) are often utilized as a variety of thin-film insulators. In turn, the semi-permeable properties of some plasma polymers allow them to be used as selective membranes. By combining the low electrical conductivity and selective permeability, one can get great barrier materials. Thus, for example, very thin barrier layers for direct methanol fuel cells (DMFC) were produced. For the technical realization of the DMFC, a highly proton conducting polymer electrolyte is necessary. Perfluorosulfonic acid membranes, such as Nafion®, are widely used to this end. Indeed, these membranes have high proton conductivity, but their great disadvantage is too high permeability of methanol molecules that migrate from anode to cathode lowering the cell performance. Deposition of a thin plasma polymer film, produced by PECVD from perfluoroheptane (C_7F_{16}), on the membrane surface decreases the methanol permeability by two-orders of magnitudes (Lue et al., 2007).

The possibility of plasma copolymerization and the production of composite materials allows to design at the molecular level thin films of very low electronic conductivity, but with very high ionic conductivity. Such films can be obtained in the polymer-like form (polymer electrolytes) and as ionic glasses (solid oxide electrolytes). These new solid electrolyte systems enable us to replace the conventional solid electrolytes by the much thinner elements, which in addition have all the other advantages of plasma fabricated materials, for example, selective permeability. Thin films of solid electrolytes produced by cold plasma deposition techniques have been of particular interest recently.

6.1 Solid electrolytes for fuel cells

The most common polymer electrolytes (often called the ion-exchange membranes) for fuel cells are composed of crosslinked macromolecular chains making up a three-dimensional structure on which are distributed some ionizable functional groups giving the membrane its specificity. To maintain the electroneutrality of the material, ionized sites are compensated for by an equivalent number of mobile ions of opposite charge. By jumping between ionized sites, these mobile ions give the membrane its ionic conduction ability. To prepare ion-exchange membranes by plasma polymerization, it is necessary first to choose a precursor with long and flexible chains or, at best, containing spacers in its structure (phenyl groups, for example) and then to initiate the deposition process with a "soft" plasma discharge in order to safely preserve those elements of the precursor likely to constitute the skeleton of the final material. The next criterion, namely, a large quantity of ionizable functional groups favorably distributed in the polymer matrix, requires the selection of a second precursor containing the appropriate ionizable functional group in its structure, which will be embedded in the polymer matrix without defects. A schematic representation of basic processes that occur in the "soft" plasma polymerization of a proton-exchange membrane from styrene and trifluoromethane sulfonic acid (CF_3SO_3H) is shown in Fig. 14.

The first works devoted to the development of plasma-polymerized ion-exchange membranes for fuel cells were carried out in the late 1980's by the Inagaki's group at the Shizuoka University in Japan (Inagaki, 1996). Plasma polymerization of a mixture of fluorinated benzene (C_6F_6, C_6F_5H or $C_6F_4H_2$) and SO_2 gave a Nafion®-like plasma polymer that contains sulfonic acid and sulfonate groups. Such a membrane has the cation-exchange

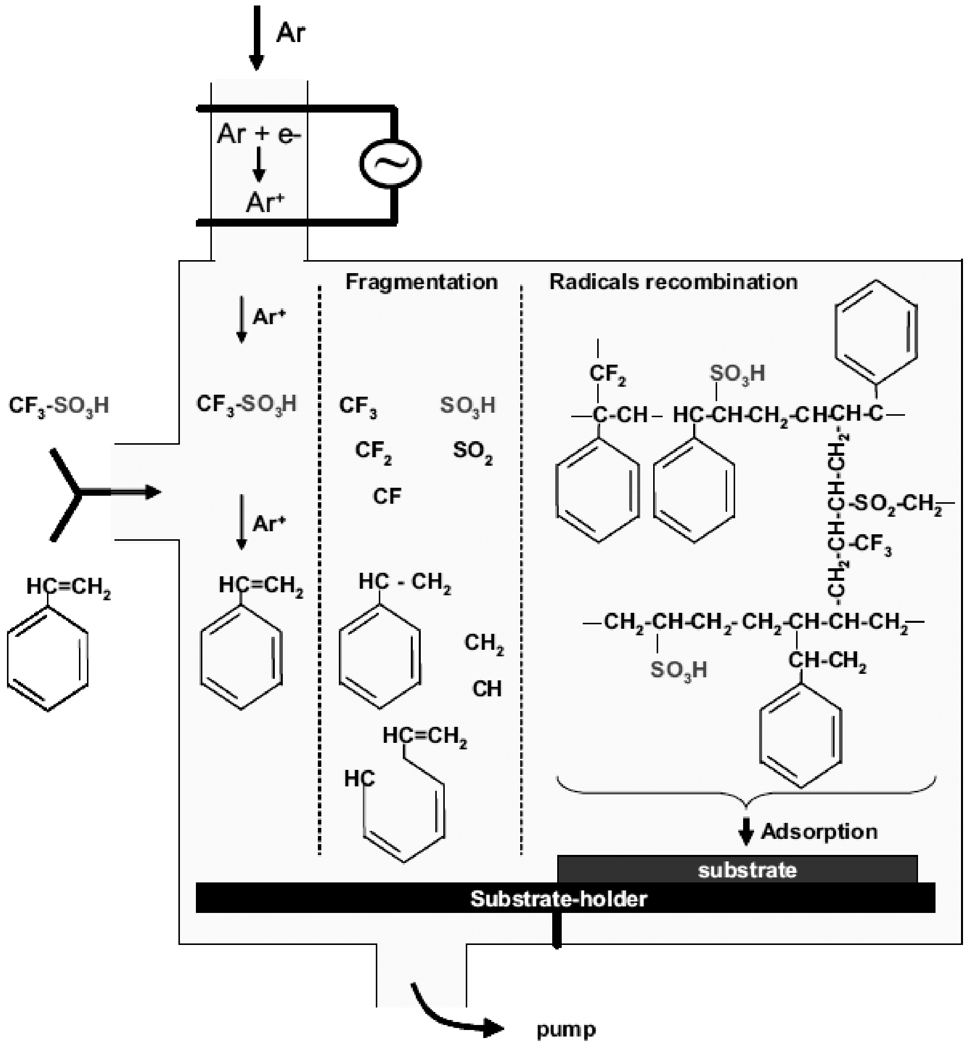

Fig. 14. Schematic representation of the synthesis procedure of proton-exchange plasma polymers (Roualdès et al., 2007).

ability and its main role is to provide the transport of protons from the anode where they are produced by the oxidation of fuel (Eqs. (5) and (7)), to the cathode where they are consumed by the reduction of oxygen into water (Eqs. (6) and (8)). Until recently, the results obtained in this respect were not as good as those for conventional membranes (Roualdès et al., 2007). However, the latest reports provide much more promising results. For example, the mentioned already proton-exchange membranes, which are plasma deposited from styrene and CF_3SO_3H (Fig. 14), can have a higher percentage of proton exchange groups, a higher proton conductivity and a lower fuel permeability, compared with commercially available Nafion® membranes, when appropriate parameters of the plasma process are chosen. Moreover, various plasma procedures are examined in search of these membranes with the best properties. Apart from the typical PECVD method (Ennajdaoui et al., 2010; Roualdès et al., 2007), the remote (after glow) plasma technique (Jiang et al., 2011) and the plasma deposition under high pressure conditions (Merche et al., 2010) have been employed. Other types of proton-exchange membranes prepared by cold plasma deposition, different from those from styrene and CF_3SO_3H, have also been investigated, for example, fluorinated carboxylic membranes from H_2O and C_4F_8 (Thery et al., 2010), phosphorous-doped silicon dioxide membranes from SiH_4, PH_3 and N_2O (Prakash et al., 2008) as well as membranes produced by plasma polymerization from heptylamine ($C_7H_{15}NH_2$) or 1,7-octadiene (C_8H_{14}) and then their treatment by SO_2 plasma (Siow et al., 2009).

The cold plasma technology is also tested for the preparation of anion-exchange membranes, which are presently becoming significant materials for application in alkaline fuel cells, where hydroxyl ions OH^- are the ion charge carriers. Similarly, as in the case of the proton-exchange membranes, the plasma deposition provides formation of very thin crosslinked films with high ion (OH^-) conductivity, high chemical stability and low fuel permeability. The first attempt to obtain such membranes was undertaken only in 2006, when precursors containing tertiary amine groups were plasma polymerized and then the deposited films were quaternized by methyl iodide (Schieda et al., 2006). Very recently, an opposite procedure was applied, namely, the films were plasma polymerized from vinylbenzyl chloride, then the benzyl chloride groups ($-CH_2Cl$) present in the films were quaternized by trimethylamine into $-CH_2N^+(CH_3)_3Cl^-$ groups, and finally these groups were alkalized by KOH into $-CH_2N^+(CH_3)_3OH^-$ groups. This material proves to be an excellent hydroxide ion conductor with great potential for application in alkaline direct alcohol fuel cells (Zhang et al., 2011).

Lastly, we should also mention the solid oxide fuel cells (SOFC), which are currently of great interest. As far as the plasma technology is concerned, the thermal plasma (see: Fig. 1) is particularly relevant in this case (Henne, 2007). However, the cold plasma is trying to use as well. In addition to the reactive sputtering method that is quite justified when we want to obtain thin films of inorganic oxides (e.g. La-Si-O, which is a potential candidate as electrolyte material for intermediate-temperature solid oxide fuel cells (Briois et al., 2007)), attempts to employ the PECVD method have been also made. Popular solid oxide electrolyte material including yttria-stabilized zirconia (YSZ) was prepared by microwave plasma polymerization from (acetylacetonate)zirconium(I) and tris(dipivaloylmethanato)-yttrium(III) as precursors (Itoh & Matsumoto, 1999). Recently performed physicochemical investigations of such deposited solid electrolyte films have shown characteristic nanostructures that are strongly affected by the variation of plasma parameters and the precursor mixture composition. Thus, we can obtain the films with exactly the desired structure and properties, for example, with appropriate ionic conductivity.

6.2 Solid electrolytes for lithium-ion batteries

The polymer electrolytes for Li-ion batteries are fundamentally the same as those used in fuel cells, with the only difference that ions transported in this case are Li^+ ions. These membranes should be very good electronic insulators that separate the anode from the cathode, but very good lithium-ion conductors. They should also have adequate chemical resistance as well as adequate mechanical strength to withstand the pressure changes and stresses of the electrodes during discharge/charge cycling of the battery. All these requirements can be satisfied by plasma polymerized thin films. The first reports on the preparation of such films appeared at the end of the 1980's. The films were deposited from precursors containing alkoxy, siloxane and vinyl groups in one molecule. Then, the films were sprayed with a solution of $LiOCl_4$ to introduce Li^+ into the plasma polymer structure (Ogumi et al., 1989). In subsequent years, more complex systems were prepared. For example, to suppress a reaction between electrodes and the electrolyte, especially to suppress the dendritic growth of lithium during battery charging, a concept of functional gradient solid polymer electrolyte was developed. This electrolyte system was obtained by changing the composition of the mixture of precursors (dimethyl-2-[(2-ethoxyethoxy) ethoxy]vinylsilane and 1,1-didifluoroethylene) during the plasma polymerization process (Ogumi et al., 1997).

The PECVD technique appears to be a unique method that allows for the implementation of Li-ion batteries with particularly sophisticated architecture. A new type of 3D microbatteries with anode or cathode post-arrays has been recently developed in the Tolbert Lab at University of California (Los Angeles). However, such systems require a solid electrolyte in the form of conformal coatings that will evenly cover the high aspect ratio electrodes. Plasma deposited polyethyleneoxide-like electrolyte films, which are electronic insulating and can be intercalated with lithium ions, have been chosen to this end. Currently, these films are intensively investigated (Dudek, 2011).

7. Conclusions and outlook

A huge potential for the production of new materials and control their structure lies in the cold plasma. This technology allows us to produce materials in the form of thin films or nanoparticles, with uniform or gradient construction, and with amorphous or nanocrystalline structure, which can be deposited on substrates of any shape. We can also obtain complex composites in this way. A special place among these composites is occupied by 3D systems. The plasma deposited materials may have very high or very low conductivity (both electronic and ionic), may have very high or very low permeability for a given substance and, in the end, may have surprising catalytic and photocatalytic properties. Without a doubt, the cold plasma technology has strongly consolidated its position in the fabrication of thin-film solar cells. Increasingly, however, it is also employed to produce materials for the components of fuel cells and Li-ion batteries, such as electrodes and solid electrolytes. Many times, these elements showed better properties than those prepared by conventional methods. One can expect that in the near future it will be possible to produce efficient and effective anode–(solid electrolyte)–cathode systems in one continuous process consisting of consecutive acts of plasma deposition. Such a construction will eliminate the problem, inter alia, of ensuring proper contact between the electrodes and solid electrolyte. The plasma technology also opens up prospects for the spectacular solutions, such as microbatteries with high aspect ratio electrodes or asymmetrical supercapacitors. It seems also feasible to produce miniaturized 3D cells in which electrodes are formed from carbon nanotubes decorated with nanoparticles of catalytic material (all fabricated by plasma processes), and covered with a plasma-polymer electrolyte. Indeed, the prospects are very promising.

Another issue, which is only briefly mentioned in this Chapter, is the use of cold plasma for surface modification of conventional materials. We can thus improve the properties of "conventional" elements relevant to the construction of electrochemical cells: electrode substrates, electrodes themselves, separators, etc. Research interest in this field of the cold plasma technology is comparable to that which is focused on entirely new materials produced by plasma deposition techniques. The use of the plasma treatment technique in electrochemical cell engineering is a problem, however, so vast that a separate chapter should be devoted to it.

8. Acknowledgment

I would like to thank all the members of my team: prof. P. Kazimierski, dr. S. Kuberski, dr. J. Sielski, R. Kapica, as well as my doctor students: P. Makowski, W. Redzynia, A. Twardowski, and I. Ludwiczak, for their excellent cooperation. I also thank Ms. K.M. Palinska for her technical assistant in the preparation of this Chapter.

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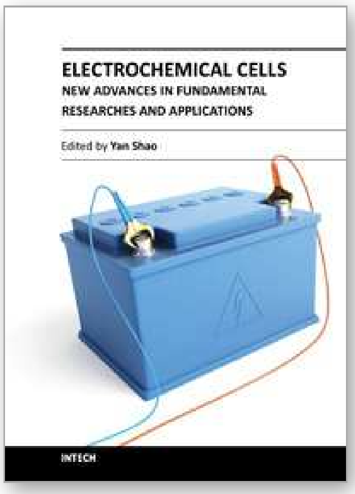

Electrochemical Cells - New Advances in Fundamental Researches and Applications
Edited by Dr. Yan Shao

ISBN 978-953-51-0032-4
Hard cover, 240 pages
Publisher InTech

Published in print edition March, 2012

Jacek Tyczkowski (2012). Cold Plasma – A Promising Tool for the Development of Electrochemical Cells, Electrochemical Cells - New Advances in Fundamental Researches and Applications, Dr. Yan Shao (Ed.), ISBN: 978-953-51-0032-4, InTech, Available from: http://www.intechopen.com/books/electrochemical-cells-new-advances-in-fundamental-researches-and-applications/cold-plasma-a-promising-tool-for-the-development-of-electrochemical-cells

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