

# NANOSTRUCTURED MATERIALS USED FOR DESIGN OF THE COMPONENTS OF FUEL CELLS

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Our targeted contribution takes into account that applications where the materials, structured at nanometric scale, can improve performances for electrodes and catalysts in fuel cells. In this context are presented some aspects where the nanotechnology is involved in fuel cells designing. In addition, are presented the requirements from the nanostructured materials with examples on several of materials produced in our laboratories. Carbon ribbons obtained from polyacrylonitrile (PAN) in the cross fields, thermal and centrifugal, are materials with a good define texture and controllable thickness 1–100 microns, designed for electrodes and the proton exchange membranes. Carbon-ribbons have of aromatic structures similar with the ladder polymers with graphite specific conduction in basal plane and specific catalytic activity. Carbonic materials with high electrical conductivity and gas permeability were obtained by the phenol-formaldehyde resin and PAN carbonizing. They have been proposed as an alternative for electrodes in fuel cells. Using plasma polymerization combined with electrospray ionization resulted nanocomposites from polymer semiconductors-nanocarbons and inorganic copolymers with catalyst insertion that could open a new route to disperse or to insert catalysts direct onto membranes or electrodes.

*Key words:* nanotechnology, nanostructured materials, fuel cells.

## 1. INTRODUCTION

We are now on the first stages of the next, and possibly most dramatic and far-reaching industrial revolution, based on the application of even smaller scale technology – nanotechnology. It is predicted that nanotechnology will have a great potential for contribution to renewable energies. Fig. 1 let us see how we can envisage the progress of nanotechnology in different areas.

The nanotechnology outputs had a powerful impact for energy, storage and conversion. There is no any component in batteries, fuel cells, hydrogen storage, supercapacitors, without nanoparticles and different carbon nanostructured materials. The most relevant effect of nanoparticles for energy applications is the large amount of the atoms exposed on the surface compared to the bulk material. The large surface area leads to a high reactivity with low material use, which is

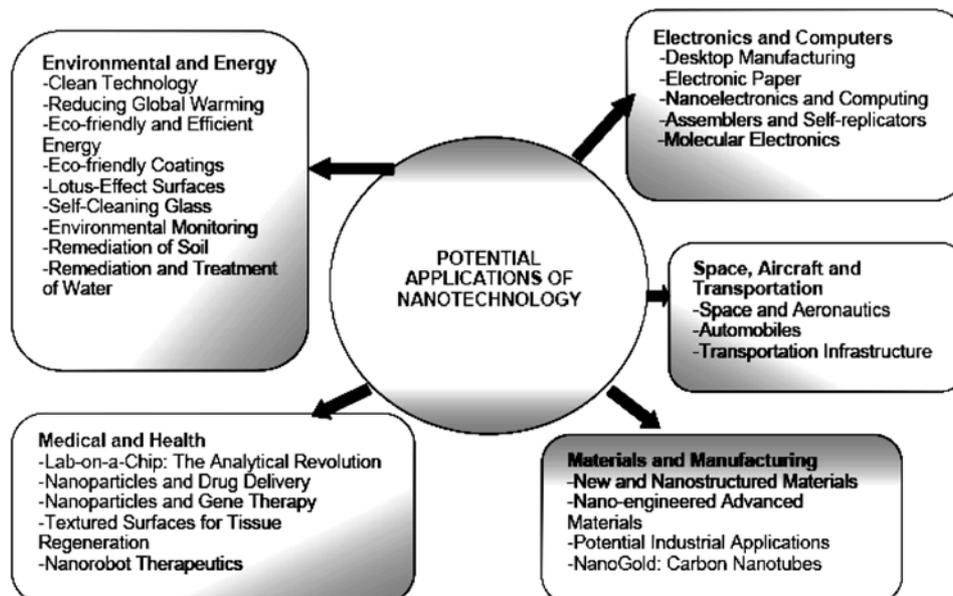


Fig. 1. – Trends of nanotechnology.

useful for better catalysts (leading to higher reaction rates, lower processing temperatures, reduced emission or need for less material), for improving combustion processes (higher efficiency, lower processing temperatures) or higher absorption rates for light. This surface effect is also relevant for energy storage applications (*e.g.*, hydrogen storage or electrodes for lithium batteries) or energy transformation (electrodes for fuel cells).

Nanomaterials possess many unique chemical, physical and mechanical properties. Due to these beneficial properties, nanomaterials are being favorably considered for a wide variety of structural, non-structural, biomedical, and microelectronic applications. Novel carbon structures and pyrolyzed polymers open opportunities for new multifunctional materials with broad applications. The assembly of nanostructured materials into functional structures is a very interesting area of the nanomaterials research. These structures may offer the greatest opportunities for highly functional devices. Matrix direct self-assembly is an efficient and rapid route to synthesize and assemble nanostructured materials into advanced devices. In addition, a wide range of nanomaterials including semiconductor, metals, ceramics, polymers photonic band gap and composites can be synthesized and assembled [1].

Most of the research activities on production and applications in fuel cells and energy devices are focused on: 1. Nanostructured materials for hydrogen storage and fuel cells; 2. Structure-property relationships in electrochemical nanomaterials; 3. Nano-catalysts for low temperature fuel cells; 4. Supported

mixed metal nanoparticles for fuel cells electrodes; 5. Zeolite nanocomposite membranes and carbon nanotube based electrodes; 6. Organic membranes for fuel cells; 7. Proton exchange membrane with nano-size proton conductor for DMFCs; 8. Fullerene nanofibers as potential materials for fuel cell electrodes; 9. Single-walled carbon nanotubes in fuel cell technologies and electrodeposited nanostructures for microfabricated fuel cells (This enumeration is not exhaustive).

The major challenges that remain will require the discovery and development of better performing materials.

## 2. FUEL CELLS: CLASSIFICATION AND ACTUAL STATUS

Fuel cells are energy conversion devices that have capability of producing electrical energy for as long as the fuel and oxidant are supplied to it and needs no slow recharging. It consists of two electrodes coated with catalyst in contact with a solid or liquid electrolyte layer who carries electrically charged particles from anode to cathode. Fuel cells generate electricity exploiting electrochemical reaction in which oxygen and hydrogen combine to form water.

The demand of high quality energy in large energetic installed power ask from science new advanced materials for high conversion yield and a powerfully integration, miniaturization and clean conditions. Fuel cells need more investigation in materials field get a high transport through electrolytes, proton exchange membranes, catalysts, electrodes, fluid transport. In addition, the choice of fuel, electrode and electrolyte materials dictates the operational temperature and therefore performance characteristics. Fuel cells benefit from electrodes and electrolytes with nanostructured and therefore enlarged surface of thin films of nanometer thickness. The most prominent nanostructured material in fuel cells is the catalyst, which consists of carbon, supported precious metal particles in the range of 1–5 nm. This structure is necessary in order to increase the surface to volume ratio of the noble metals thus reducing the costs of the material. Table 1 shows the classification and fuel cells status [2, 3].

DMFCs are a variation of the PEM type, use liquid methanol without initial reforming. The introduction of proton conducting membranes led to renewed interest in DMFCs, particularly since the elimination of a bulky fuel reformer makes them potentially more attractive than the hydrogen-fuelled cells for portable and mobile applications. One of the key points to develop a DMFC is to investigate new materials for electrodes and new electrocatalysts for the oxidation of methanol at the anode, allowing to increase the current density and to decrease the anodic over voltage. Another approach is to develop composite membranes with the dual properties of high proton conductivity and low methanol crossover. The conceptual model of DMFC, the reaction equations at electrodes and reactants together with by-products circuit are illustrated in Fig. 2 [4].

Table 1

The classification of the fuel cells

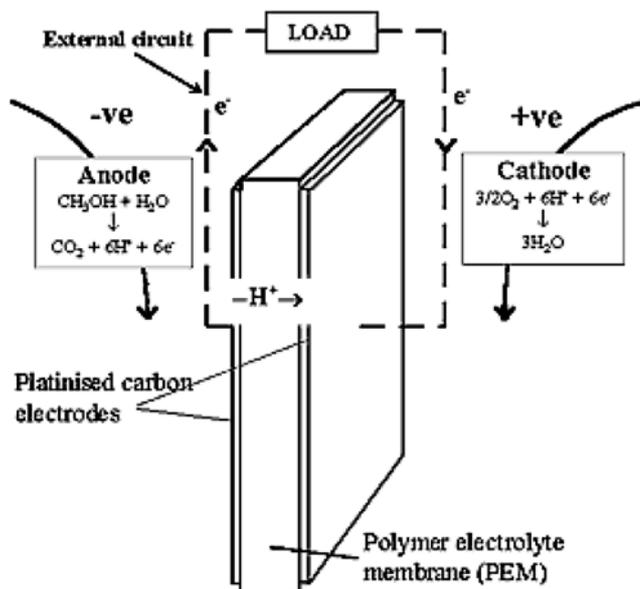
Fuel cell	Anode gas	Cathode gas	Electrolyte	Catalyst	T [°C]	Power densities [mW/cm <sup>2</sup> ]	Scale	Efficiency %
AFC	H <sub>2</sub>	pure O <sub>2</sub>	KOH	Pt	150–200	200/>300	100 W–100 kW	50–70
PEMFC	H <sub>2</sub>	O <sub>2</sub> or air	ion exchange membrane	Pt	50–80	350/>600	100 W–10 MW	40–50
PAFC	H <sub>2</sub>	air	phosphoric acid	Pt	150–220	200/250	200 kW–10 MW	35–50
DMFC	CH <sub>3</sub> OH	air	solid polymer membrane	Pt Pt/Ru Pt/Pd	50–120	40/>100	1–100 kW	35–40
MCFC	H <sub>2</sub> or CH <sub>4</sub>	air	Li-K-carbonate/ LiAlO <sub>4</sub> matrix	Ni	600–650	100/>200	1–100 MW	50–60
SOFC	H <sub>2</sub> or CH <sub>4</sub>	air	ceramic oxide	Perovskites	600–1000	240/300	100 kW–100 MW	50–60

AFC – the alkaline fuel cell (transport), PEMFC – proton exchange membrane fuel cell (space travel small CHP mobile equipment), PAFC – phosphoric acid fuel cell (power plants CHP), DMFC – direct methanol fuel cell (transport mobile equipment), MCFC – the molten carbonate fuel cell (power plants CHP), SOFC – the solid oxide fuel cell (power plants CHP).

One of the key points to develop a DMFC is to investigate new electrocatalysts for the oxidation of methanol at the anode, allowing to increase the current density and to decrease the anodic over voltage. Platinum is widely used in catalysts and electrocatalysts. Methanol oxidation on a Pt surface is incomplete and generates intermediate species such as CO or COH ( $\text{CH}_3\text{OH} \rightarrow \text{COH(ads)} + 3\text{H}^+ + 3\text{e}^-$  or  $\text{CH}_3\text{OH} \rightarrow \text{CO(ads)} + 4\text{H}^+ + 4\text{e}^-$ ) which can poison the catalyst [5]. Several studies have shown that the best electrocatalyst for methanol oxidation is a platinum-ruthenium system, with Ru who serves the role

of removing CO (abs) as CO<sub>2</sub> (gas), binary Pt and Ru catalysts the order of catalytic activity for these binary alloy catalysts is Pt-Ru > Pt-Os > Pt-Ag > Pt-Rh [6].

Fig. 2. – Direct methanol fuel cell- functional principle.



### 3. NANOSTRUCTURED MATERIALS FOR FUEL CELLS

The long experience accumulated in fuel cells, established the requirements to reach conversion efficiency close to the theoretical predicted one. The catalysts and the diffusion layer between electrodes and electrolytes must have a specific area on volume unit very large. The catalyst poisoning due to carbon monoxide need a fast removing of the gases from the contact surface. The proton mobility through membrane or electrolyte must be comparable with the electron mobility in the external circuit. The hydrophobicity of membrane should be accommodating with the rate of the water releasing. The electrodes must have low electrical resistance and high permeability for fluids. These effects on each component of fuel cell are opposite. To design a specific material with these properties need a real skill art. The materials appropriate with these requirements are that multifunctionals and nanostructured. Particularly with our purpose, the carbon-polymers structures satisfy many of these properties. Carbon-polymeric materials, which associate carbonic materials (from graphite, nanocarbon to fullerene and nanotubes) with polymeric matrix, used specific nanotechnologies methods such as blending, architecturing and auto-assembling are very promising for fuel cells.

These materials affiliate the specific properties of carbon with the properties of polymers and have widespread area of applications. Based on percolation

effect and the clusters assembling in the polymer structures (nanotubes, nanoshells, and new tetragonal structures, carbon-ribbon, and polymers semiconductors) the properties might be tunable in large range.

A series of materials have been developed using new methods for synthesis or processing. Thus pyrolyzing phenol-formaldehyde resins crosslinked with hexamethylenetetramine was identified a tetragonal structure with metallic properties [7–9]. In the same way, polyacrylonitrile was pyrolyzed in centrifugal field and a series of ladder polymers were obtained [10]. Using plasma polymerization combined with electrospray ionization resulted nanocomposites from polymer semiconductors – nanocarbons and inorganic copolymers with catalyst insertion. Shortly these materials are presented in the next sections with evaluation as potential applications to fuel cells components.

#### 4. NEW MATERIALS FOR ELECTRODES AND MEMBRANES IN FUEL CELL

**Tetragonal carbon structures.** In the previously work, we reported a new method of synthesis for silicon dicarbide and glitter structures with a spiroconjugation structures as provided by Bucknum [8, 11]. These novel materials were synthesized from bulk pyrolysis of Novolac resin (a phenol-formaldehyde resin similar to Bakelite) together with hexamethylenetetramine (HMTA) as a crosslinking agent and micron-sized silicon.

*Glitter* is a heretofore-hypothetical tetragonal allotrope of carbon first reported in 1994, as a theoretical construction, by Bucknum and Hoffmann. The lattice parameters for glitter are,  $a = 2.53 \text{ \AA}$  and  $c = 5.98 \text{ \AA}$ , the density is  $3.12 \text{ g/cm}^3$  [12].

*Silicon dicarbide* is isostructural with the previously elucidated hypothetical carbon allotrope glitter. It is a tetragonal structure with  $a = 3.07 \text{ \AA}$  and  $c = 7.02 \text{ \AA}$  and lies in space group P42/mmc, like glitter, with six atoms in the unit of pattern. The density of silicon dicarbide is  $2.61 \text{ g/cm}^3$  [13].

These structures are metallic and hard three-dimensional extended structure. Theoretical calculations of the zero-pressure bulk modulus of  $\text{SiC}_2$  is one of the highest known in crystalline materials at 230 GPa and for glitter this analysis indicates that the zero-pressure bulk modulus of glitter is nearly the same as that in the diamond lattice [12, 13]. Due to metallic behavior, these structures are potential electrode materials in fuel cell.

**Pyrolyzed polymers.** Pyrolyzed polyacrylonitrile (PAN) in simultaneous thermal and centrifugal field, developed films with micron thickness and composition of large oriented ladder polymers (made of pyridine cycles). Continuing pyrolysis to  $1000^\circ\text{C}$  has been obtained carbon-ribbon similar in

structure with carbon fibers [10]. These materials have proved a very good behavior in electrical conductivity, the rate of fluid diffusion/migration catalyst adherence.

Electrical properties (Table 2) of these pyrolyzed polymer and rate of liquid diffusion through these materials were measured in bulk samples using homemade equipments.

Table 2

Electrical properties

Samples	$\sigma \cdot 10^3$ [S·cm <sup>-1</sup> ]
Novolac resin with HMTA 10%wt (reported at novolac resin)	7.1
Novolac resin with HMTA 10%wt and Si 10% (reported at novolac resin)	13.5
PAN	36.1

Carbonic materials with high conductivity and low polarization, obtained by carbonizing novolac and PAN are potential competitors for electrodes in micro direct methanol fuel cells. All materials examined by our group (carbonized novolac with HMTA, carbonized novolac and Si with HMTA, carbonized PAN) shown that the conversion of novolac and polyacrylonitrile at 900°C and chemical catalyst deposition can be proposed as another route for the electrodes for fuel cells having good physical properties (such as electrical conductivity, the rate of fluid diffusion/migration).

Electrical conductivity and rate of liquid diffusion through these materials show the highest rate of the fluid penetration and PAN is the best conductive [14].

The graphic representation:

$$\ln(Q_{\max} - Q) = f(t) \quad (1)$$

where  $Q = m - m_0/m_0$ , gives rise to the migration/diffusion rate,  $K$  (s<sup>-1</sup>), which values were plotted in Fig. 3.

The overall results clearly indicate better characteristics and performance for these electrodes.

**Carbon ribbons** obtained from polyacrylonitrile (PAN) in the cross-fields thermal and centrifugal are materials with very high specific area, designed for electrodes and the proton exchange membranes in fuel cells. The carbon fibers scalable to micro and nanoscale and structured in different matrix or activated remain the best competitors in field. High electrical conductivity along a direction coupled with high permeability for fluids in perpendicular direction are required in electrodes for fuel cells. In membranes, need hydrophobicity and high mobility for protons. Carbon ribbons meet these requirements [14]. This technique allowed the achievement of PAN/Novolac-carbon ribbons deposited onto Al-foil with a good definite texture and a controllable thickness of

1–100 microns. Carbon-ribbons are made of aromatic structures of carbon similarly the ladder polymers with graphite specific conduction in basal plane and specific catalytic activity.

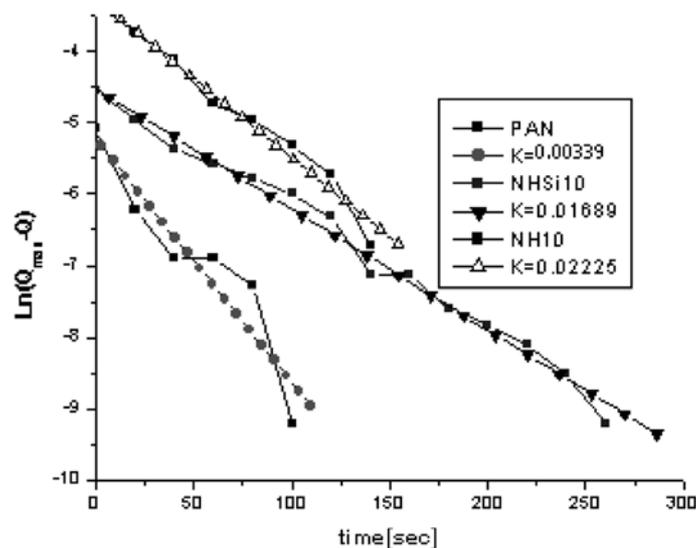


Fig. 3

**Nanocarbon-polymer semiconductor nanocomposites.** Well known the plasma polymerization has not been appropriate to produce polymers close in characteristics with the chemical synthesis. Recently our developments in reactor design using electrospray ionization have been deposited films of polyaniline with nanocarbon. The method opened a new route to disperse or to insert catalysts direct onto membranes or electrodes [15, 16].

## 5. CONCLUSIONS

A series of materials synthesized by new methods have been presented as an alternative to improve characteristics and performances for fuel cells. These materials show high molecular orientation and large capacity of the fluid transport. They can be designed in different configurations.

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