

STRUCTURAL ASPECTS OF FUEL CELL ELECTRODES

E. Budevski*

Central Laboratory of Electrochemical Power Sources, Bulgarian Academy of Sciences,
Sofia 1113, Bulgaria

The development of gas diffusion electrodes for fuel cells and hybrid metal air batteries based on the experience of the Central Laboratory of Electrochemical Power Sources will be shortly reviewed. The application of new materials particularly PEM will be given. The promise of new composite materials based on carbon nanotubes and proton conductive polymers will be discussed.

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1. Introduction

It is out of question that the ultimate solution for energy production, saving and conversion is the use of the renewable energy sources, and particularly next to wind and wave power the solar photo-voltaic hydrogen production and energy conversion cycle.

Next to the photo-voltaic energy conversion itself, the main problem in this cycle arises from the hydrogen energy conversion in the so called fuel cells. Here I would like to discuss the problems connected with the proton exchange membrane fuel cell (PEMFC) as the most advanced and promising fuel cell version. In general structural aspects will be scrutinized.

2. The classical H₂/O₂ fuel cell

The classical fuel cell uses aqueous (liquid) electrolytes and gas diffusion electrodes for the hydrogen oxidation and the oxygen reduction water producing process in order to convert the chemical to electrical energy. It is a three phase system, gas-liquid-gas, the phases being separated by the gas diffusion electrodes (GDE)

The gas diffusion electrode takes several functions:

- First, the confinement of the liquid electrolyte within the electrolytic cell separating the liquid ion conducting media from the gaseous reactants: the oxygen and the hydrogen.
- Second, it offers a highly developed liquid-gas-electrode three phase boundary where the electrode reactions take place.
- Third, it serves as a carrier of the catalysts ensuring a fast electron exchange reaction.
- Fourth, it provides for a fast transportation of the reactants and the reaction products to and from the three phase boundary,
- Finally it ensures a fast lateral electron transportation.

The requirements are quite severe for the transportation processes having in mind that from a square centimeter of electrode surface area a current of the order of 1 A is expected with an ohmic loss of less than 100-200 mV. This electrode reaction rate corresponds to roughly 0.7 W cm⁻² specific power generation.

* Corresponding author: budevski@bas.bg

The classical solution of the gas diffusion electrodes from the sixties of the last century is given in Fig. 1. As an example the very rigid electrode structure as developed in the Central Laboratory of Electrochemical Power Sources in Sofia is demonstrated [1-4].

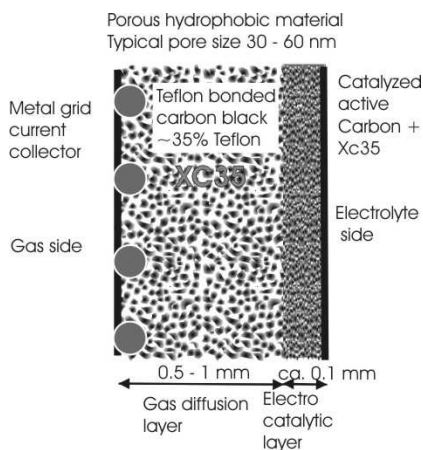


Fig. 1. Structure of a gas diffusion electrode of the 60-ties (CLEPS – BAS)

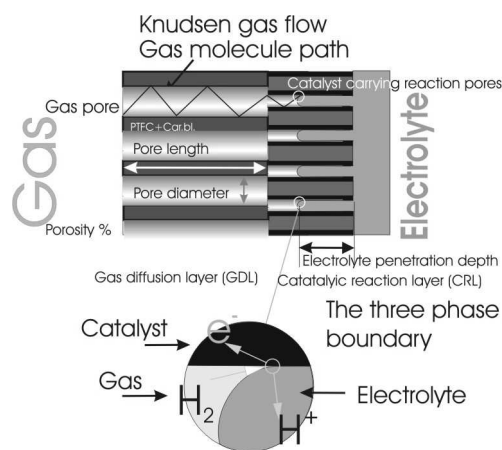


Fig. 2. The theoretical model and the three phase boundary.

The main structural element of the electrode is the Carbon Black 35 % PTFC bonded layer (Material known as XC35 or XC72 in the *de Nora* E-Tek nomenclature) of a thickness of 0.5 to 1 mm. It is characterized by a high porosity (typically 60 %), high hydrophobicity over 8000 leak proof working hours, good electronic conductivity and extremely low pore diameter (typically 30 to 60 nm). It has been shown that due this small pore size the gas transport is predominantly Knudsen flow type of diffusion insensitive to the presence of additional gases. A theoretical model is given on Fig. 2. The theory was developed by Iliev and Kaischeva [5 - 7]. This theory played a leading role for the development and the many applications of the Bulgarian GDE.

On the gas side the layer is reinforced by an iron grid thus rendering an additional conductivity and strength to the sheet. The electrolyte side is covered by a mixture of XC35 with catalyzed active carbon containing a low amount of PTFC. The catalyzed aggregates are therefore hydrophilic. The electro-catalytic layer is ca. 0.1 mm thick. This structure insures a highly developed three phase boundary for the electrode reaction.

Oxygen (air) gas diffusion electrodes have been used for more than 20 years in different application mainly in metal air throw away or mechanically rechargeable batteries. The electrolyte is usually highly concentrated KOH water solution.

As an air electrode the GDE it is operating for more than 8000 to 10000 hours at $200 \text{ mA} \cdot \text{cm}^{-2}$ at room temperatures. It shows a good performance even at low temperatures down to $-10^0 \text{ } ^\circ\text{C}$, insensitive to the presence of CO_2 [8]. Several applications developed in CLEPS BAS are given below [9 –14]:

- A rechargeable iron air battery using a third electrode for charging the iron electrode (1968).
- Cadmium air battery powering an indoor electric truck (1969).
- Mechanically rechargeable 220 V Zinc-Air battery experimented on a Mosquich converted electric car (1969).
- A series of throw-away 1.5 V, 120 to 5000 Ah zinc-air batteries for technical and military applications having in been in production for 4 years (1980).
- A throw-away 1.5 V, 3000 Ah zinc-air battery in regular production for 4-5 years in Mussala a Samokov BG factory for powering marine light buoys. 4 years export – Stralsund, GDR (1981).

In general the classical type of the fuel cell is quite bulky and complicated system very sensitive to the technological process and water leakage during operation.

3. The proton exchange membrane fuel cell

Some 30 years ago Dupont created a perfluorosulfonic acid/PTFE copolymer in the acid (H^+) form, commercially available as Nafion in different grades [15].

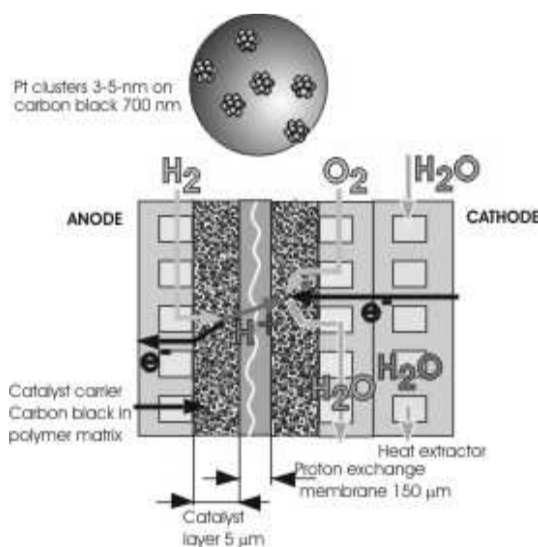


Fig. 3. An advanced version of a catalyst coated PEM cell assembly.

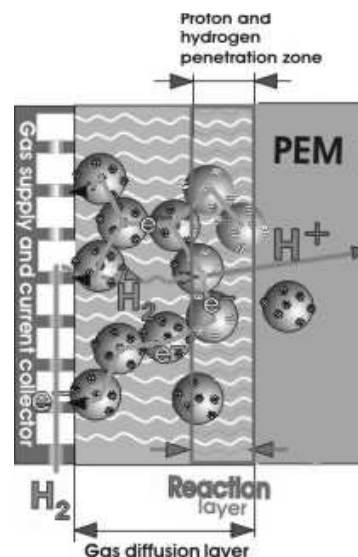


Fig. 4. Model of the electro-catalytic layer of a CCM.

DuPont's Nafion® PFSA membranes are non-reinforced films based on Nafion® PFSA polymer. Nafion® PFSA membranes are widely used for Proton Exchange Membrane (PEM) fuel cells and water electrolyzers. The membrane operates as a separator and solid electrolyte in a variety of electrochemical cells which require the membrane to selectively transport cations across the cell junction. The polymer is chemically resistant and durable.

The use of a solid polymer electrolyte eliminates the need of a water tight compartment for the liquid electrolyte and, the corrosion and safety concerns associated with it, Fig. 3. Thus the thick water proof XC35 gas diffusion layer is eliminated. The electro catalytic layer is replaced by a thin sheet of porous, graphitized paper which has previously been wet-proofed with Teflon. The catalyst, usually platinum, is deposited as nano sized clusters (3 – 5 nm) on a carbon support – carbon black particles (ca 0.7 – 1 μm) and embedded one-sided into the graphitized paper sheet. Two sheets are applied both-sides to the membrane forming the cathodic and anodic catalyzed layers. This PEM assembly is known as *catalyst coated membrane* (CCM) assembly.

The graphitized paper sheet can be eliminated completely if the catalyst is applied to form a thicker (5 μm) electro conductive catalyst layer on the membrane, with a sacrifice of performance efficiency of the Pt catalyst.

Fig. 4 shows an advanced Membrane Electrode Assembly – MEA, using CCM. The gas supply and the electron collection is ensured by a profiled gas conducting plate forming the outer confinement of the single cell.

Gas is supplied laterally from the electrode borders to the inside of the electrode compartment, while electrons are transported in normal direction by the conductive plate to the next cell. At higher power densities an additional electro conductive plate with a water cooling channel system is inserted between every two adjacent cells.

The proton exchange membrane Nafion typically operates below 70-85 °C. Its low operating temperature provides instant start-up and requires no thermal shielding to protect personnel. About 50% of maximum power is available immediately at room temperature. Full operating power is available within about 3 minutes under normal conditions. Recent advances in performance and design offer the possibility of lower cost than any other fuel cell system.

A model of the electro catalytic layer is given in Fig.4. The power generation obviously takes place only on selected sites where hydrogen can be transported and the protons can be accepted and transported away. The carbon black particles transport by contact the electrons to the next particles and to the current collector plate. The reaction itself can proceed only where hydrogen (gas phase) and protons (solid or electrolyte) are available, and the electrons made free can be transported away by an electro conducting chain of carbon particles.

It is clearly seen how little from the Pt catalyst can be used effectively in this constriction. Still up to 0.5 A cm^{-2} at 0.7 V are reported. This corresponds to roughly 0.35 W cm^{-2} at loads not exceeding $0.2 \text{ mgr Pt per cm}^2$.

At present, Nafion-type membranes dominate the commercial market. These membranes meet many of the needs described above yet have perceived or real shortcomings. These shortcomings include high cost, unacceptable methanol cross-over and water transport rate, and completely inadequate properties above 100°C , an important emerging condition for which membranes will be used. In an attempt to fill these gaps, several new materials have emerged.

4. New materials in PEMFC

4.1. The proton conductive membrane

The most advanced membrane materials are grafted or doped copolymers of Polybenzimidazole (PBI) [16 – 25]. The material has been studied for almost one decade in the Case Western Reserve University in Cleveland. Major contributions are given by the school of R. Savinell. PBI is produced and distributed solely by Celanese USA. A battery is now under development at Celanese Ventures Hoechst Frankfurt.

PBI is a temperature and electricity insulating material, highly chemically and temperature resistive. It is stable at temperatures as high as 350°C and above. It does not melt. Mechanically it is as strong as steel. PBI shows a selective proton conductivity which can be increased by grafting or doping of acidic groups [17 to 19].

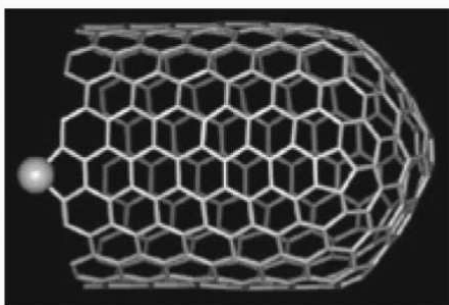


Fig. 5. Single wall nanotube (SWNT).

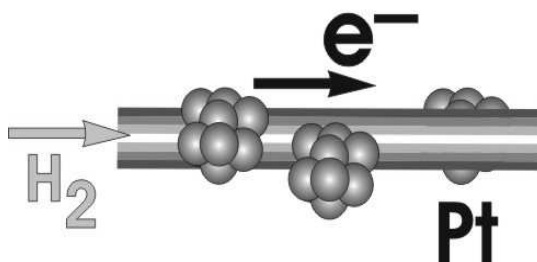


Fig. 6. Catalyst loaded carbon nanotube.

PBI and its copolymers are soluble in some organic solvents and can be drawn from solution to threads or formed to membranes. The use of novel PCM can dramatically improve the performance of PEMFC particularly at higher temperatures. With PBI or related materials specific power densities of the order of 1 W cm^{-2} can be expected.

4.2. Carbon nanotubes

Up to now as catalyst carrier materials sub-micro sized carbon materials have been used, preferably carbon black. In-between new materials such as nano-sized carbon or other materials, e. g. Bucky type materials fullerenes or carbon nano tubes have emerged. As catalyst carriers this materials

could provide not only for a higher chemical and mechanical stability, higher electrical conductivity, but also higher developed interphase boundary.

I would not like to repeat what is already well known from the literature. An excellent review by P. Holister, T. Haper and Cr. Roman Vas appeared recently, published as a white paper by CMP Cientifica (www.cmp-cientifica.com) in January 2003 under the title Nano Tubes [26]. I only wish to repeat some sentences taken from this paper:

“Carbon nanotubes are one of the most commonly mentioned building blocks of nanotechnology. With one hundred times the tensile strength of steel, thermal conductivity better than all but the purest diamond, and electrical conductivity similar to copper, but with the ability to carry much higher currents, they seem to be a wonder material.”

From the whole arsenal of nano-tubes, nano-horns, fullerene, carbon nano-fibers the best choice, for an illustration like this at least, would be single walled carbon nanotubes, SWNT as given in the drawing Fig. 5. A tube by itself would offer gas transport channels. SWNT have a diameter of nano meters. The tube volume is almost inaccessible for other materials and can not be filled except with gases. At the same time the walls apparently show a good permeability of atomic hydrogen. SWNT can be obtained as long as 100 to 1000 nm. With this length a tube can penetrate the entire reaction layer and will render good breathing conditions for the whole layer.

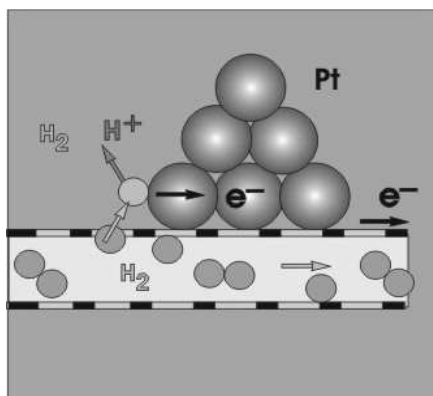


Fig. 7. Catalyst loaded SWNT.

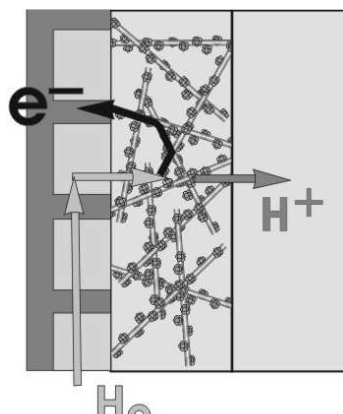


Fig. 8. Integrated breathing reaction layer in an electrode assembly.

If on the outer surface of the tubes, catalyst clusters are deposited, and the fibers - catalyst loaded SWNT (Fig. 7), are embedded in a proton conductive polymer matrix forming a thin layer, than this layer can be easily sealed to a proton conductive membrane of the same material (Fig. 8).

Thus the PE membrane can be double sided coated with a composite material of this kind to form the gas evolution and gas consuming reaction layers. The integrated breathing reaction layer IBRL is schematically shown on Fig. 8. The IBRL obviously can effectively replace the gas diffusion - reaction layer double layered structure of CCM. It can be clearly seen that the Pt utilization can be expected to be roughly 100%. The thickness of the IBRL can be dimensioned according to the power density needs. A peeling of the IBRL from the substrate is hardly to be expected if the same PCM is used for the IBRL matrix and the membrane.

The nanosize effect. The catalyst carrier being of the size of nano meters can bring additional nanosize effects. The distances between the catalyzed fibers are now so small that even if a catalyst particle has lost its direct contact with the carrier electron tunneling can be expected making isolated catalyst particles effective. Hydrogen can be supplied in this case by the tubes and by short distance diffusion.

5. Outlook and research needs

As seen the use of novel Bucky type, particularly tubular materials, can be expected to enhance significantly the performance characteristics of the MEA and the catalyst effectiveness of

the IBRL itself. Use of carbon nanotubes such as nanohorns in fuel cell electrodes has been reported elsewhere [27]. A preparation technology suitable for IBRL has been reported recently [28].

Any way a number of questions and problems must be solved before an IBRL assembly can be brought into live:

- Firstly a feasibility experimental study for the use and benefits of carbon fibrous or nano tube materials.
- The electrochemistry of the catalytic electrode hydrogen oxidation and oxygen reduction reactions may be changed completely making our water electrochemistry experience obsolete.
- The whole development of the solid electrolyte is in a very early stage and new inventions can be expected.
- Almost nothing is certain about production, properties and preparation technologies of carbon nano tubes and related materials.
- In addition we are entering a new world of nano dimensions where almost nothing can be predicted.

These could be the few but substantial problems that the IBRL assembly is imposing on science, experiment and technology.

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