

Simulation of PEMFC with Pt/CNT Nanostructured Cathode Catalyst

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By using CFD methods, we carried out simulation of the phenomena occurring in the hydrogen-air fuel cell. As a result of this modeling we obtained the calculated discharge curves data of two fuel cells with two cathodes catalysts types 20PtE-TEK (0.42 mg_{Pt}/cm²) commercial catalyst and catalytic system synthesized on carbon nanotubes (CNT+15%XC72). The calculated values do agree with the experimental data. The calculations made in accordance with the mathematical model have showed that the nanostructured synthesized catalyst is more stable than the commercial one under prolonged testing. Synthesized CNT-based catalyst systems can be a good alternative to the commercial catalysts.

1. Introduction

The technology of Proton Exchange Membrane Fuel Cells (PEMFC) is one of the most perspective and fastest developing tendency in power engineering. Fuel Cells (FC) are used as a power source for electronic devices, vehicles, aircraft, equipment. Currently commercially available Fuel Cells use platinum as the catalyst and carbon black as its support.

However, the application of this metal leads to a number of significant problems preventing from mass usage of FC. Firstly, it is a sufficiently high cost of platinum, which has a greater impact on the cost of the Membrane-Electrode Assemblies (MEA) production. Secondly, the drawback of the commercial catalyst system is its low stability: "irrevocable" platinum dissolution in surrounding polymer electrolyte with high acidity and corrosion of the carbon medium.

The latest developments in the field of catalysts for the MEA of FC are aimed at creating new systems with high activity and stability. Thus, the increase of FC working resource is one of the most topical issues of electrochemical energy.

2. Experimental studies of CNT based FC cathode catalysts

The laboratory of electrocatalysis and fuel cells of the A.N. Frumkin Institute of Physical chemistry and Electrochemistry RAS (Moscow, Russia) and its employees have been working on creation of anode and cathode catalysts based on the CNTs and platinum modified with nitrogen and transition metals (Mn, Mo, Ni, etc.) respectively in order to increase their corrosion resistance compared to pure platinum and carbon black (Bogdanovskaya et al., 2011).

Within the framework of the joint work Ms. Bogdanovskaya and others have developed an effective liquid-phase polyol synthesis method of monoplatinum catalyst on CNT, with platinum content of 20 wt%, which enables, in the model conditions, to obtain the platinum surface of 45 - 50 m²/g and the activity in electro-reduction oxygen reaction of ~ 50 A/g at the potential of 0.9 V, while maintaining high selectivity with regard to recovering oxygen to the water and higher stability.

The laboratory carried out tests of CNT synthesis catalysts in the MEA structure.

Formation of the MEA was based on the method proposed for forming the commercial monoplatinum catalyst Pt/C based MEA (Avakov et al., 2014). This method involves several steps: preparation of catalytic inks,

application of cathode catalyst layer, application of anode catalyst layer, mechanical, thermal and chemical treatment of the obtained membrane with application of catalyst layers (Catalyst Coated Membrane (CCM)), connection of Gas Diffusion Layers (GDL) and gaskets to CCM with receipt (production) of MEA.

The corrosion test of MEA with catalysts containing 20 wt% Pt (commercial and nanotube based) has been carried out by using the express testing (voltage cycling) with potentials range of 0.6 - 1.1 and 0.6 - 1.3 V. The voltage cycling has been carried out with scan rate of 0.10 V/s. The detailed methodology of accelerated testing by the method of voltage cycling and determination of the MEA characteristics at various process stages is presented in the work of Avakov et al. (2014)

Besides when making research into the catalyst synthesized by the polyol method, a carbon black XC72 agent was introduced into CNT to provide electronic conductivity through the thickness of the active layer.

A part of the experimental data is shown in the Figures 1-3 of the section 4.

3. Computer simulation of the FC

Simulation of the hydrodynamic and physico-chemical phenomena occurring in the FC has been carried out with the help of Computational Fluid Dynamics (CFD) methods with the use of commercial software FLUENT ANSYS. The mathematical model, as well as an algorithm for constructing of FC geometric model were presented and tested by the authors in their previous works (Vasilenko et al., Koltsova et al.).

The mathematical model is found on the solution of the basic CFD equations describing the phenomena occurring in all areas of FC: mass conservation (continuity) equation, momentum conservation, species conservation and charge balances.

The model takes into account the influence of the active Electrochemical Surface Area (ECSA), platinum content in the Active Catalyst Layer, FC dimensional characteristics on current and power values generated by the FC.

The species conservation equation in the GDL accounting gas humidification can be represented as follows:

$$\frac{\partial(\varepsilon \rho_j \vec{v} (1-\lambda) c_j)}{\partial t} + \nabla \cdot (\rho_j \vec{v} (1-\lambda) c_j) = \nabla \cdot (\rho_j D_j \nabla c_j) \quad (1)$$

in which ε – porosity, ration of pore volume to zone volume $\varepsilon = \frac{V_{pore}}{V_{zone}}$, V_{pore} – the total volume of two phase

medium (m^3), V_{zone} – the total volume of three phase porous system (m^3), ρ – species density (kg/m^3); \vec{v} – velocity vector of the fluid (m/s), λ – water content, ratio of liquid water volume to two phase medium volume; D_j – species diffusion coefficient (m^2/s), c_j – species concentration, (mol/m^2), j – hydrogen at the anode, oxygen at the cathode.

In the active catalyst layer species concentrations at the anode and the cathode are determined by the relationship:

$$\frac{\partial(\varepsilon \rho_j (1-\lambda) c_j)}{\partial t} + \nabla \cdot (\rho_j \vec{v} (1-\lambda) c_j) = \nabla \cdot (\rho_j D_j \nabla c_j) + \frac{M_j}{n_j F} i_{an,cat} \quad (2)$$

in which M_j – molecular weight of species j (kg/mol), n_j – number of electrons taking part in the reactions, i – current density per volume (A/m^3), low indexes an, cat associated with values of anode or cathode areas respectively.

The diffusion coefficient in the gas phase is given in accordance with approach published by Sukkee Um et al:

$$D_j = \varepsilon^{1.5} (1-s)^{r_s} D_j^0 \left(\frac{P_0}{P}\right)^{\gamma_p} \left(\frac{T}{T_0}\right)^{\gamma_t} \quad (3)$$

in which D_j^0 – the mass diffusivity of species j at reference temperature and pressure (P_0 , T_0) (m^2/s), r_s -- the exponent of pore blockage, $r_s = 2.5$, $P_0 = 101,325$ (Pa), $T_0 = 300$ (K); $\gamma_p = 1.0$; $\gamma_t = 1.5$.

Charge balance should be taken into account in addition to the equations of mass, momentum and species conservation.

The equation of charge conservation is determining equation that describes the transfer current. The equations for two processes are solved in the model. The Eq(4) represents the electrons e^- transport through electron-conducting solid materials (for example, current collectors and solid supports (carbon materials) of catalysts). The Eq(5) describes the protons H^+ transfer process.

$$\nabla \cdot (\sigma_{sol} \nabla E_{sol}) = S_{sol} \quad (4)$$

$$\nabla \cdot (\sigma_{mem} \nabla E_{mem}) = S_{mem} \quad (5)$$

in which σ – electrical conductivity, (1/($\Omega \cdot m$)); $E_{sol,mem}$ – potencial (V) of solid phase or membrane; $S_{sol,mem}$ – source/sink term characterizing current density per volume in solid phase or membrane (A/m^3). At the anode $S_{sol} = -i_{an}$, $S_{mem} = i_{an}$, at the cathode $S_{sol} = i_{cat}$, $S_{mem} = -i_{cat}$.

An additional complication is in the fact that the electrical conductivity of the ionomer, σ_{mem} depends on temperature and water content in the membrane λ , corresponding to the number of water molecules per one sulfonic acid group $\lambda = \frac{N_{moleculesH_2O}}{N_{sulphergroup}}$. According the model of Springer et al. λ is a function of the

experimental conditions (relative humidity) out the membrane area.

Generating fluxes of electrons or ions are equal in any volume of active anode or cathode, i.e. $S_{sol} = S_{mem}$. Moreover, the total current (either electrons or ions) generated in the anode catalyst layer must be equal to the total current consumed in the cathode catalyst layer, and must be equal to the total current flowing through the membrane.

Thus the equation of charge conservation should be accounted at simulation:

$$\int_{an} i_{an} dV = \int_{cat} i_{cat} dV \quad (6)$$

The electric current is generated by the electrochemical reactions occurring at the catalyst surface. Kinetic driving force is the local surface overpotential η_{act} (V), also known as activation losses. As a rule it is the difference between the solid and membrane potentials, E_{sol} and E_{mem} .

$$\eta_{act,an} = E_{sol} - E_{mem} \quad (7)$$

The change of electric potential in transition from the anode to the cathode can be accounted by subtracting of the open circuit voltage V_{oc} from the cathode side.

$$\eta_{act,cat} = E_{sol} - E_{mem} - V_{oc} \quad (8)$$

The electrochemical reactions rates of hydrogen oxidation at the anode and oxygen reduction at the cathode are described by the Butler-Volmer equation (9, 10). The electrochemical reactions rate, expressed as current density on the anode and cathode, depends on ECSA, platinum loading and overvoltage at the anode and the cathode.

$$i_{an} = \frac{S_{an} m_{Pt}}{V_{AL}} i_{an}^{ref} \left(\frac{c_{H_2}}{c^{ref}_{H_2}} \right)^{\gamma_{an}} \left(e^{\alpha_{an} F \eta_{act,an} / (RT)} - e^{-\alpha_{cat} F \eta_{act,cat} / (RT)} \right) \quad (9)$$

$$i_{cat} = \frac{S_{cat} m_{Pt}}{V_{AL}} i_{cat}^{ref} \left(\frac{c_{O_2}}{c^{ref}_{O_2}} \right)^{\gamma_{cat}} \left(-e^{\alpha_{an} F \eta_{act,an} / (RT)} + e^{-\alpha_{cat} F \eta_{act,cat} / (RT)} \right) \quad (10)$$

in which S – ECSA (m_{Pt}^2/kg_{Pt}); m_{Pt} – platinum loading in the active catalyst layer (kg_{Pt}); V_{AL} – volume of active layer, (m^3); i^{ref} – reference exchange current density per unit of platinum active surface area (A/m^2_{Pt}), (at the temperature 25 °C and pressure 101.325 kPa); c^{ref}_j – reference species concentration (mol/m^3); γ – stoichiometric ratio, reaction order; α – transfer coefficient, η_{act} – local activation overpotential (V); F – Faraday constant (C/mol); R – universal gas constant (J/(mol K)); T – temperature (K).

4. Results of computer modeling

In general, the process of computer simulation of FC can be schematically divided into the following phases: construction of the geometric model; the geometric model splitting into finite elements, the construction of the computational grid; determination of the model areas and boundaries (areas of solid and gas-liquid phases, inlet and outlet gas supply system and gas channels, walls, places of layers combinations, places of electrode contacts); setting of boundary conditions and calculating parameters; calculation; visualization of calculated results.

The process of the mesh generation is an integral part of any computer calculation that uses Computer-Aided Engineering (CAE) technology. The quality of built computational grid has direct influence on the speed of computational experiment solution, the accuracy and the convergence of the results. The FC geometric model and the calculating grid consisting of 7 million elements have been constructed. Tetrahedral elements have been used for mesh model construction of gas supply channels, GDL and bipolar plates, and hexahedral elements have been used for the active layers and the membrane.

The discharge characteristics of fuel cells with two types of catalysts: synthesized nanotubes-based catalyst (CNT+15%XC72R) and the commercial monoplatinum catalyst 20PtE-TEK ($0.42 \text{ mg}_{\text{Pt}}/\text{cm}^2$) have been obtained due to calculations based on the mathematical model.

Figure 1 shows the calculated and experimentally measured discharge curves. Presented graph shows that there is a good agreement between the calculated and experimental data.

However, there were difficulties in obtaining the calculated curves for experiments with air as the oxidant at the cathode. One can see (Figure 1) that in these cases there is a sharp decrease in the values of the potential at high values of current density. That fact is explained by increasing of transport losses, due to formation of so-called "nitric pad" in the active and gas diffusion layers at the cathode side, that blocks oxygen access to the active centers of the catalyst. Therefore, it was necessary to make adjustments to the calculated data obtained for the case with pure oxygen. Calculation of transport losses was carried out according to the method proposed by Arisetty et al. In order to obtain the "true" value of voltage for experiments with air as the oxidant, calculated transport losses values have been subtracted from data obtained for pure oxygen at the corresponding value of the current density. At the same time in areas with low values of current density, transport losses are not taken into account and assumed to be zero $\eta_{tr} \approx 0$.

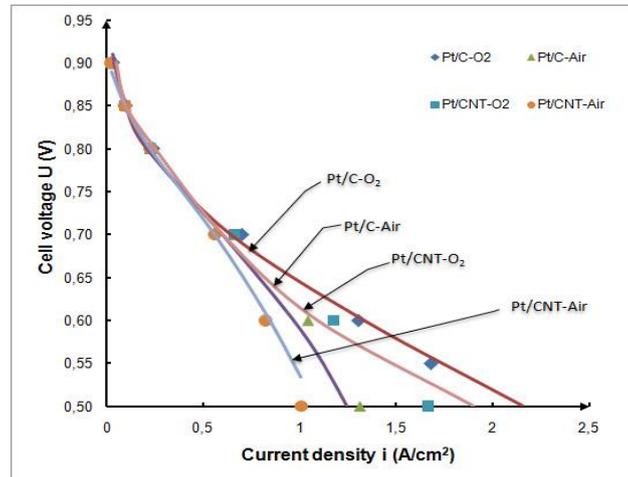


Figure 1: Comparison of the calculated and experimental discharge curves. The curves show calculated results; the dots show experimental data. Pressure is 2 atm in all cases.

Table 1 shows the values of some parameters of the cathode and the anode used in the modeling of the MEA with different cathode catalysts.

Table 1: Characteristics of MEA cathode and the anode with different cathode catalysts

Parameter	Anode Pt 9100 ($0.32 \text{ mg}/\text{cm}^2$), N/C 1.0 cathode 20PtE-TEK ($0.42 \text{ mg}_{\text{Pt}}/\text{cm}^2$)		Anode Pt 9100 ($0.32 \text{ mg}/\text{cm}^2$), N/C 1.0 cathode 20Pt (CNT+15%XC72R) ($0.45 \text{ mg}_{\text{Pt}}/\text{cm}^2$)	
	Anode	Cathode	Anode	Cathode
$i^{\text{ref}}, \text{ A}/\text{cm}^2$	5,000	10	5,000	8
α	0.5	0.5	0.5	0.5
γ	0.6	0.6	0.6	0.6
$S, \text{ m}^2\text{Pt}/\text{g}_{\text{Pt}}$	24	58.13	24	20.26

In order to determine the stability of the catalysts we have calculated prediction values of ECSA at greater than in the tests conducted number of cycles (5,000).

Regression dependencies for experimental data have been obtained to calculate ECSA:

$$S = ae^{bN} \quad (11)$$

in which a , b – regression coefficients, N – number of cycles. The values of the regression coefficients (11) are shown in Table 2.

Figure 2 shows the catalysts ECSA values calculated due to the regression Eq(11) including greater cycles number (5,000), at which the tests haven't been carried out.

Despite the fact that the initial ECSA of commercial catalyst is in three times higher the corresponding value of the synthesized catalyst, after 2,000 cycles of testing active catalyst surfaces are equal. Further comparison of the curves shows that at 5,000 cycles active surface of commercial catalyst is reducing more than 95%, while reduction of synthesized catalyst ECSA is less than 50 %.

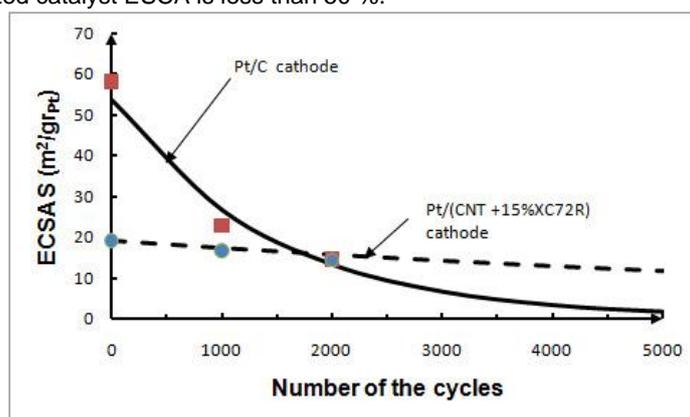


Figure 2: Calculation of ECSA at 5,000 cycles. The dots show the experimental data: ■ - for the MEA with the commercial catalyst on the cathode; ● for the MEA with the synthesized catalyst on the cathode.

The predicted (with the help of the mathematical modeling) at 5,000 cycles discharge curves for the MEAs with the commercial and synthesized CNT-based catalyst cathodes are shown in Figure 3.

Comparison of calculated voltage curves for two catalysts shows that before cycling the characteristics of CNT-based catalyst are similar to the commercial catalyst in high-voltage area, and in the area of high current density they are lower only by 8-10% compared to commercial one. However, predicted by mathematical modeling the voltage characteristics of the synthesized catalyst are significantly higher than those for commercial one after 5,000 cycles. The predicted reduction of discharge characteristics of the synthesized CNT catalyst at high current density area is about 10% after 5,000 cycles.

Thus, the results of experimental studies and mathematical modeling has showed that the nanostructured catalyst synthesized by polyol method is more stable than the commercial one after conducting more than 2,000 cycles. Synthesized CNT-based catalyst systems show higher stability and can be a good alternative to the commercial catalysts.

5. Conclusions

The paper presents the mathematical model of a hydrogen-air fuel cell. The model has been built upon the basis of Computational Fluid Dynamics methods.

The general equations of the mathematical model are the equations of mass conservation (equation of continuity), momentum conservation, species conservation, as well as charge conservation.

Calculated discharge curves data of two fuel cells with two cathodes catalysts types 20PtE-TEK (0.42 mg_{Pt}/cm²) commercial catalyst and catalytic system synthesized on carbon nanotubes 20Pt/(CNT+15%XC72R) (0.45 mg_{Pt}/cm²) have been obtained due to the mathematical model. The calculated values are in good agreement with the experimental data.

With the help of the regression dependency based on the measured data ECSA predicted values of 5,000 cycles have been calculated.

Calculations carried out according to the mathematical model have showed that the nanostructured synthesized catalyst is more stable than the commercial one after prolonged tests. Synthesized CNT-based catalyst systems can be a good alternative to the commercial catalysts.

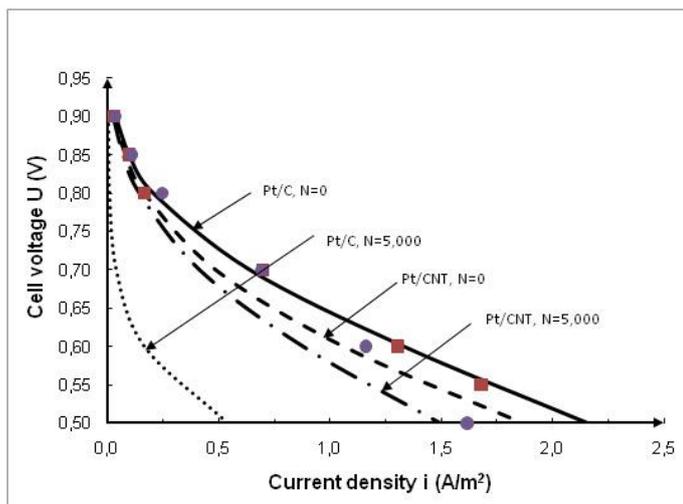


Figure 3. Comparison of the calculated discharge curves for the MEA with the catalysts of 2 types before cycling ($N = 0$) and after 5,000 cycles. The dots show the experimental data before cycling: ■ - for the MEA with the commercial catalyst on the cathode; ● for the MEA with the synthesized catalyst on the cathode.

Table 2: The values of the regression coefficients (11) for various MEA catalysts

Catalyst	Regression coefficients	
	a	b
Commercial 20PtE-TEK	53.554	$-7 \cdot 10^{-2}$
Synthesized 20Pt CNT+15%XC72R	19.252	$-1 \cdot 10^{-3}$

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