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Flicker Noise Spectroscopy in the Analysis of Electrochemical Noise of Hydrogen-air PEM Fuel Cell During its Degradation

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A variation in fluctuation dynamics of the noise component of the electric potential of a fuel cell was studied. A fuel cell with polymer membrane and gas diffusion layer was tested and treated with a fast degradation procedure. The characteristics of electrochemical noise were obtained using a flicker noise spectroscopy that provides an analysis of a cosine-spectrum of autocorrelation function and second order difference moment of voltage noise. A sequence of fast degradation steps results in a change of maximum load current of a polymer electrolyte membrane fuel cell. The main effect of fast degradation on the noise parameters is the change in the ratio of areas (i.e. power) of the low-frequency peak (a range of $\Delta f_{LF} = 0.001 – 0.003$ Hz) to the high-frequency peak (a range of $\Delta f_{HF} = 0.258 – 0.262$ Hz) in cosine-spectrum of the autocorrelation function.

Keywords: Fuel cell, degradation, electrochemical noise, flicker noise spectroscopy.

1. INTRODUCTION

In stationary conditions, an electrochemical system inevitably generates noise as fluctuations of rates of direct and reverse electrochemical reactions. If the system is neither stationary nor uniform than the noise of voltage (or current) observed on the electrodes contains information about the microstructure of near surface layers of electrodes and about a variation of this structure with time. An interest in such noise usually arises during investigations of corrosion processes as in laboratory research and in practical problem solving [1].

The main goal of the present study is the establishment of application possibilities of electrochemical noise for the analysis of the functional condition of fuel cells (FC) with polymer electrolyte membrane (PEM). A relatively fast degradation changes in FCs is the main obstacle (besides high cost) for their wide application. Therefore, noise analysis and information that can be derived from it look in this case very promising because (i) noise measurement is a nondestructive method, (ii) it does not require equipment for high load currents, (iii) the measurement itself takes a little time. One should also bear in mind that the electrochemical system does not substantially change during fuel cell operation as it takes place for other electrochemical power sources (EPS) such as batteries and accumulators in which the chemical content of electrodes changes during discharge.

Unfortunately, some difficulties arise during measurement of EPS noise in contrast to corrosion noise: a very small signal of several microvolts is to be measured on the background of EPS voltage of about 1 volt. Moreover, the real open circuit voltage is affected by the drift of several millivolts, and this drift is also to be subtracted to obtain the noise itself. In the course of our study, we found out that there is no commercial device for electrochemical noise measurement with sufficient resolution and dynamic range. This fact was mentioned earlier by other authors [2]. Consequently, all the measurements were carried out using a device specially manufactured for this purpose by Elins Ltd.

Since a problem of understanding of particular mechanisms of the electrochemical noise generation appears to be too sophisticated [3], a phenomenological approach to searching the parameters, representing meaningful prognostic information, seems to be quite appropriate. Respectively, a method of flicker-noise spectroscopy (FNS) is such a general phenomenological approach, not requiring information on particular microscopic processes in a system [4-9].

In the present work, we used the phenomenological analysis as the principal one. It included a search for the changes in spectral and correlation characteristics of electrochemical noise containing the information about PEMFC degradation. At this, the main attention was paid to the registered changes characteristic of the system under study in low- and high-frequency components of the power spectrum of the noise at various stages of degradation. Also, the changes in the parameters of the chaotic noise, which are usually associated with anomalous diffusion, intermittency and signal bursts.

2. EXPERIMENTAL

2.1. Materials and methods

Laboratory samples of a fuel cell with a polymer electrolyte membrane were the subject of investigation. The measurements were carried out with a single fuel cell with working area of 1 cm^2. Membrane electrode assembly samples (MEA) were prepared by the most famous method on the basis of polymer membrane and gas diffusion electrodes. Polymer Nafion® NRE-212 served as the membrane. The electrodes itself were prepared by well-known Wilson's spray-technique [10, 11]. For their preparation, we used the Toray® gas diffusion carbon paper and E-TEK® catalyst (10% Pt on Vulcan® XC-72 carbon black). The catalyst was coated onto the paper as the ultrasonically produced spray using a Prism-300 system. Experimental MEA's were assembled by hot pressing the prepared catalytic electrodes with the membrane. Assembled MEA's we placed in a test cell (FC-01-02, Electrochem Inc.)/

For the electrochemical measurements (as CVA procedures and electrochemical noise measuring) the cell was placed in a hard electromagnetic shield (Faraday cage) and connected to a test set for controlled supply of gas with controlled humidity and temperature measurement. The electromagnetic screen provides full protection from interference, which was controlled by measuring the wire resistor noise (with the inherent noise of the measuring instrument).

During measurements, gaseous compartments of the cell were filled with the working , i.e. hydrogen and air. Hydrogen was produced by a TsvetChrome Ltd laboratory generator of pure hydrogen. The air was supplied by an air pump. The gasses were humidified up to 100% of relative humidity at room temperature.

To study the effect of a fuel cell aging, we used the procedure of forced degradation. The procedure of forced degradation includes repeatedly potential cycling in a range from – 1 V to 1 V for 50 times, i.e. a cyclic voltammetry technique (CV) with the potential maximum, slightly higher than FC EMF, was used. Every stage of aging was applied for four times, so we obtained a set of different aging steps for each sample. Under this exposure processes of platinum and carbon carrier electro-oxidation is active. Such exposure simulates the corrosive electrochemical processes at the cathode during long work of the FC. The procedure of forced degradation is described in detail in Russian [12].

To monitor the degree of degradation we were using the following method. Since the really fuel cell was used for the experiment, it was natural to investigate the fall of its power in operating mode. To evaluate this parameter we picked up the load characteristic using CV technique, feeding of hydrogen and oxygen at the anode to the cathode. The load characteristics of a fuel cell were obtained by potential cycling from the open circuit potential to 0.4 V with a scan rate of 0.05 V/s (during 4 cycles). The end value of the last scan at 0.4 V was used as a maximum load current and a significative of degradation degree for comparison with the data of noise analysis. As the digital significative we took the ratio of maximum current of freshly mounted FC to maximum current after each step of degradation.

The electrochemical noise was measured for an unloaded fuel cell in operation mode with hydrogen and air supplied to it. In these conditions, the open circuit potential was close to 1 V. Condition of electrodes also was monitored by potential cycling and impedance measurements were held using an Elins P-50X potentiostat-galvanostat supplied with a FRA module. By impedance spectra, we estimated the increase in the Faraday resistance, but it was small, and we did not use it as an indicator of the degree of degradation.

The electrochemical noise was measured with a specially constructed high-resolution device by Elins Ltd. The input range of this device is from –4 V to 4 V; analog to digital converter resolution is more than 24 bits; sample rate is up to 10 points per second; self-noise is smaller than 2 microvolts peak to peak and has a uniform frequency distribution throughout the range used; input impedance more than 100 GOhms.

2.2. Noise analysis. Fundamentals of Flicker noise analysis

There are two steps requires in order to an analysis of the recorded FC electrochemical noise. At the stage of preliminary signal processing, it is necessary to remove a DC component (up to 1 V that 10^4-10^5 times greater than the amplitude of the electrochemical noise) and its slow drift. In a second step, we searched for correlations and frequency characteristics of the noise associated with the aging of the fuel cell.

The first stage is a conventional one in electrochemical noise measurements, and there are invited a large number of mathematical algorithms to execute it [13]. However, after several attempts, we decided on the method of subtracting the baseline drift obtained by Savitsky-Golay approximation. This filter accurately tracks the drift, even with sharp direction changes, and does not add quasi-periodic artifacts to the noise signal, like polynomial fitting. On the other hand, it does not subtract the "intermittency" although differentiates hops. The window size for Savitsky- Golay filter was selected as 501 samples, that allow getting a noise with the spectrum down to 10^{-3} Hz after subtracting the baseline.

The second stage usually uses spectral analysis, i.e. Fourier transform of the measured signal to the analysis of spectral components.

We used more complex correlational approach, developed by one of the authors, and called "flicker noise spectroscopy" (FNS). This approach eliminates the main limitation of direct spectral analysis [14], related to the need of the Fourier transform of a non-stationary signal and irreproducibility spectral characteristics as a result.

Flicker noise spectroscopy (FNS) is a general phenomenological framework for extracting information from stochastic signals represented as a series of discrete samples on the time interval T. The parameters introduced in FNS are related to the autocorrelation function (a notation in integral form is provided, all the equations in discrete form can be found in [7, 9]:

$$\psi(\tau) = \langle V(t) V(t+\tau) \rangle_{T-\tau}, \qquad \langle (\ldots) \rangle_{T-\tau} = \frac{1}{T-\tau} \int_0^{T-\tau} (\ldots) \mathrm{d}t, \tag{1}$$

where τ is the parameter of time delay, at assumption $0 \le \tau \le T_M$ ($T_M \le T/2$).

First of all, we analyzed the cosine transform $S(f)$ (where f denotes frequency):

$$S(f) = 2 \int_0^{T_M} \langle V(t) V(t+t_1) \rangle_{T-\tau} \cos(2\pi f t_1) \mathrm{d}t_1 \tag{2}$$

and a difference moment (transitional Kolmogorov structure function) $\Phi^{(2)}(\tau)$ of the 2nd order:

$$\Phi^{(2)}(\tau) = \left\langle [V(t) - V(t+\tau)]^2 \right\rangle_{T-\tau} \tag{3}$$

The investigated noise is generated by electrochemical systems that are thermodynamically open ones. $S(f)$ is the power spectrum in the case of stationary signal and unlimited integration interval according to the Wiener-Khinchin theorem [15]. Also chaotic components there are frequencies specific for the investigated signal in the spectrum; that is «resonances» and contributions of their interference. The rest part of the $S(f)$ spectrum consists of the chaotic signal; for which a monotonous dependence on frequency is typical [16]. There is also an inevitable intermittency of the considered dynamics in these chaotic signal [9]. In general, such dynamics is represented as a sequence of time intervals on which a dynamic variable $V(t)$ changes slowly enough in a manner of random walk (presented by a sequence of «irregularities-hops») and relatively short time intervals on which variable $V(t)$ changes sharply and chaotically («irregularities-splashes»).

Such a character is typical for the signals produced by complex open systems. Analysis of $\Phi^{(2)}(\tau)$ in FNS method is caused by this intermittent dynamics. Accordingly, for the analysis of these dynamics, $\Phi_c^{(2)}(\tau)$ can be approximated as [7, 9]:

$$\Phi_c^{(2)}(\tau) \approx 2\sigma^2 \cdot \left[1 - \Gamma^{-1}(H_1) \cdot \Gamma(H_1, \tau / T_1)\right]^2, \Gamma(s, x) = \int_x^{\infty} \exp(-t) \cdot t^{s-1} \mathrm{d}t, \quad \Gamma(s) = \Gamma(s, 0), \tag{4}$$

where Γ(s) and Γ(s, x) are gamma-function and incomplete gamma-function, respectively ($x \geq 0$ and $s > 0$); σ is a root-mean-square deviation of the obtained dynamic value as the «irregularities-hops» measure of chaotic signal component; H_1 is Hurst constant which characterizes the rate at which the dynamic variable loss a memory about its value in the time intervals less than T_1. The approximation parameters σ, H_1, T_1 have been included in the analysis of experimental data.

To estimate a total chaotic contribution to the power spectrum determined by «irregularities-hops» and «irregularities-splashes» the following interpolation equation is convenient to use:

$$S_c(f) \approx \frac{S_c(0)}{1 + (2\pi f T_0)^n}, \tag{5}$$

where $S_c(0)$, T_0 and n are phenomenological parameters introduced to describe power spectra while processing experimentally obtained time series. As the measure of a chaotic signal component formed by «irregularities-hops» and «irregularities-splashes» in the region of high frequencies a parameter $S_c(T_0^{-1})$ is convenient to choose. It can be denoted as a «spikiness factor» [4, 5, 9]. So, the parameters T_0 and $S_c(T_0^{-1})$ have been included in consideration too.

As a result, the experimentally recorded noise was represented as a linear superposition of a «high frequency» chaotic component $V_c(t)$ and a slowly changing «resonance» component $V_r(t)$:

$$V(t) = V_c(t) + V_r(t).$$

In this case autocorrelation function and power spectrum can be presented as:

$$\psi(\tau) = \psi_r(\tau) + \psi_c(\tau),$$

$$S(f) = S_c(f) + S_r(f). \tag{6}$$

and [7, 8, 9]:

$$\Phi_c^{(2)}(\tau) = \Phi^{(2)}(\tau) - \Phi_r^{(2)}(\tau). \tag{7}$$

where $\Phi_r^{(2)}(\tau)$ is the resonance component.

The expressions (6, 7) allow to divide the contributions from resonance and chaotic components successfully and investigate these components separately [3, 7].

3. RESULTS AND DISCUSSION

Fig. 1 shows the initial signal (the drift of baseline is only observed visually in the Fig. 1A) and the drift resulted from smoothing with Savitzky-Golay filter (Fig. 1B). The noise of a fuel cell obtained by drift subtraction is presented in the Fig. 2. Noise power spectrum $S(f)$ for one sample of a fuel cell in the course of its degradation is demonstrated in the Fig. 3. The Fig. 4 shows CVs for a fuel cell tested in the regime of estimation of its load characteristics (see «Materials and methods»).

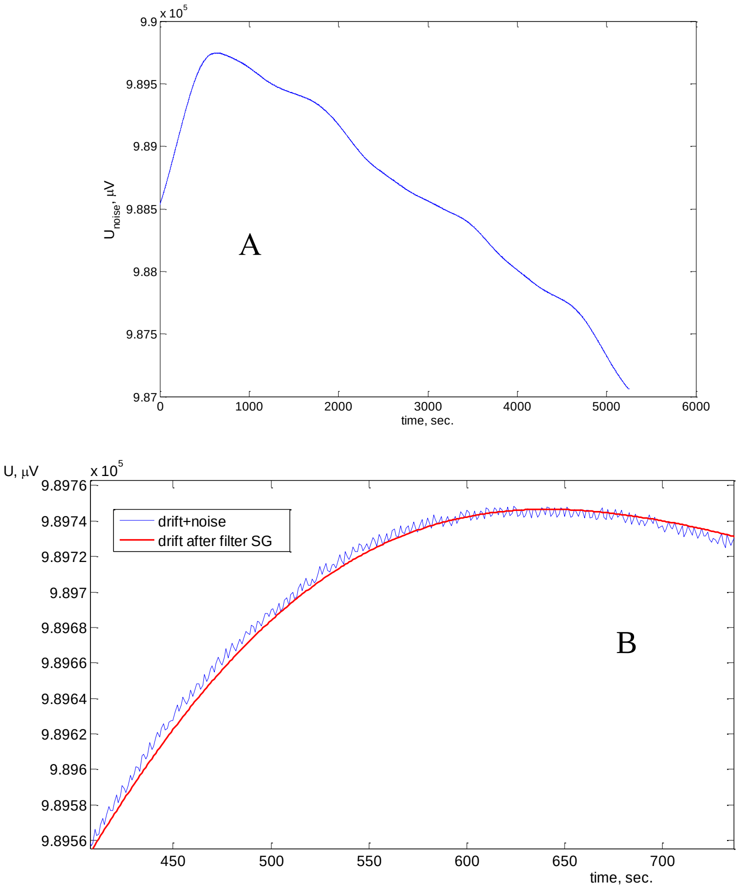

Figure 1. Initial signal of the voltage measured on the PEMFC electrodes (A). A zoomed-out view of the voltage signal (B): signal and baseline drift approximation.

For nondegraded fuel cells, load currents were observed to increase after the first aging stage. This is a widely observed effect [17] evidently caused by some catalyst activation (e.g. the contamination dissolution) that exceed the effect of initial degradation.

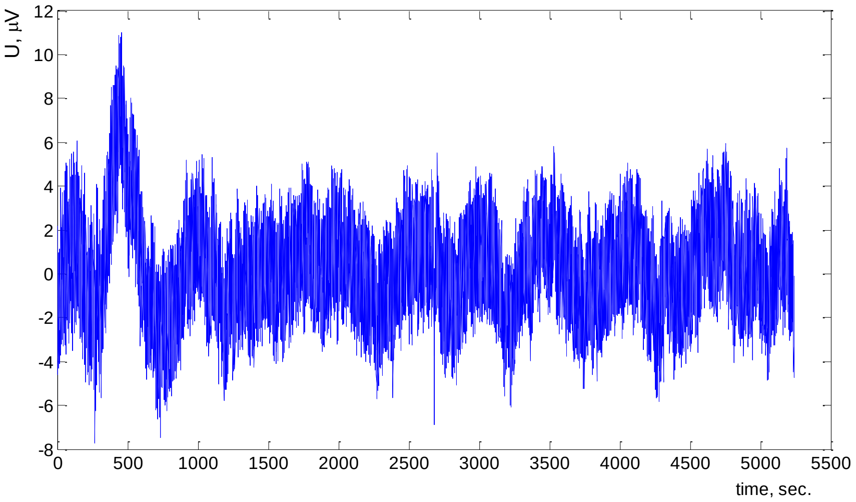

Figure 2. Noise signal measured on the PEMFC electrodes after baseline subtraction.

Consequently, as the indicator of FC degradation degree not the number n of completed stages of forced degradation was used but a ratio k_{Dn} of maximum load currents (current value at the potential of 400 mV, i.e. the outermost point to the left on the cycle in Fig. 4). So k_{Dn} denotes the ratio of the load current I_n after corresponding degradation stage to the load current I_0 of a nondegraded fuel cell:

$$k_{Dn} = I_n/I_0. \tag{8}$$

After the first degradation cycle, this value, i.e. k_{D1} is increased to some extent. After further stages of forced degradation (in our case at $n = 2 – 4$) load currents decrease and the «degradation degree» k_{Dn} diminishes. For the degradation procedure used in the present study (a cycling toward high potential that exceeds the oxidation one, i.e. in the range from –1 to 1 V) the worsening of FC parameters (load current) is connected, first of all, with the destruction of cathode nanostructure while it is affected by oxidation processes to a lesser degree. The membrane resistance does not change too; the fact was controlled using impedance spectroscopy.

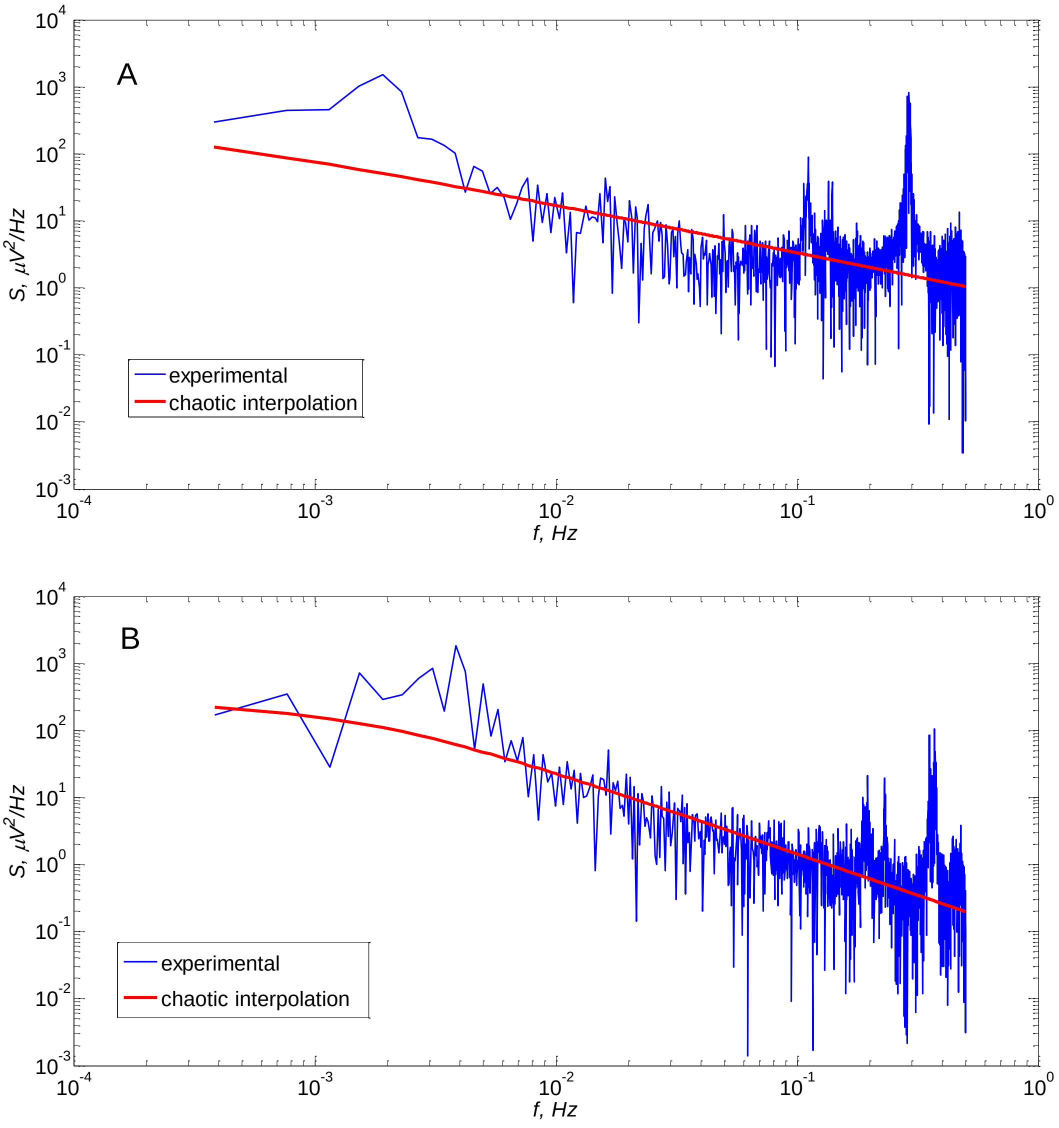

Figure 3. The changes in noise power spectrum $S(f)$ for one sample of a fuel cell in the course of its degradation: A – before degradation, B – after 4-th degradation circles.

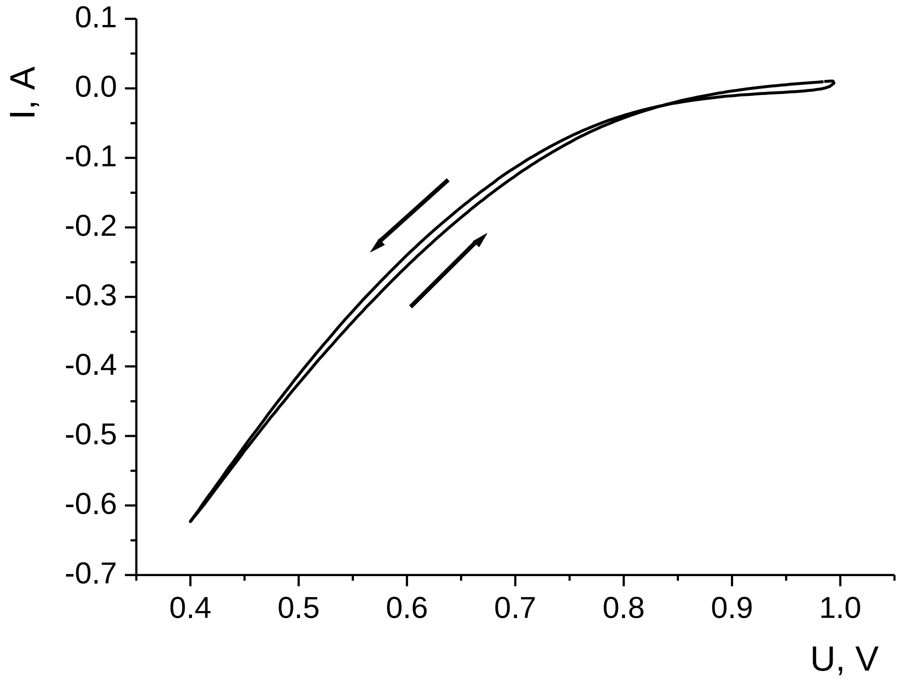

Figure 4. PEMFC load characteristics obtained by the CV method (arrows indicate the direction of potential scan). The value of current at 0.4 V was taken for analysis.

The FNS analysis of noise signal consists in the search for regularities in FNS parameters namely the magnitude of autocorrelation function cosine spectrum (noise «power spectrum») and the difference moment of the 2nd order. During such an analysis, base changes in the electrochemical noise of measured potential connected with the noise power spectrum that changed after each cycle of forced degradation were established. The power spectrum demonstrated two specific peaks namely in the region of low (a range of Δf_{LF} = 0.001 – 0.003 Hz) and high (a range of Δf_{HF} = 0.258 – 0.262 Hz) frequencies (Fig. 5). The ratio of the areas of low-frequency S_{LF} and high-frequency S_{HF} peaks:

$$\eta = \int_{\Delta f_{LF}} S_{LF}(f)df \Big/ \int_{\Delta f_{HF}} S_{HF}(f)df \qquad (9)$$

appeared to change simultaneously with the registered current ratio I_n / I_0 (Fig. 6). Such a correlation of the variations in current ratio k_{Dn} and mentioned areas can point to the structural changes in catalytic layer. The latter can be caused or by the removal of the smallest platinum particles as a result of the support oxidation either by the transport of platinum ions from smaller metal particles (2–3 nm) to larger agglomerates of catalyst present on the electrode surface as can be seen from scanning electron microscopy (SEM) images (Fig. 7). An increase in average size of platinum particles that is aggregation also results in the decrease in catalytic activity [18].

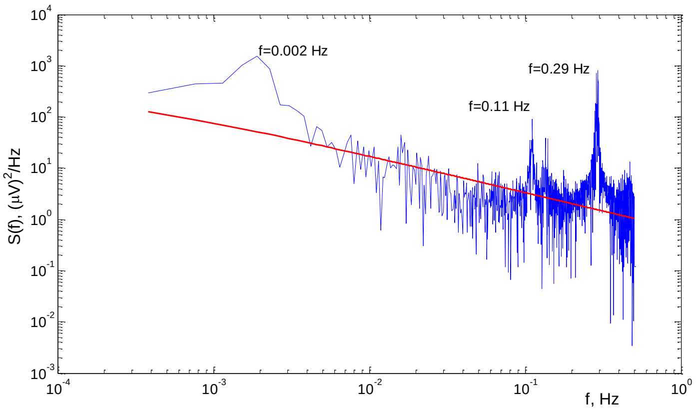

Figure 5. The spectral power density of PEMFC noise before degradation procedure. The ratio of peak area $\int_{\Delta f_{LF}} S_{LF}(f)df$ near f = 0.002 Hz to the area $\int_{\Delta f_{HF}} S_{HF}(f)df$ near f = 0.29 Hz was taken as the base characteristics.

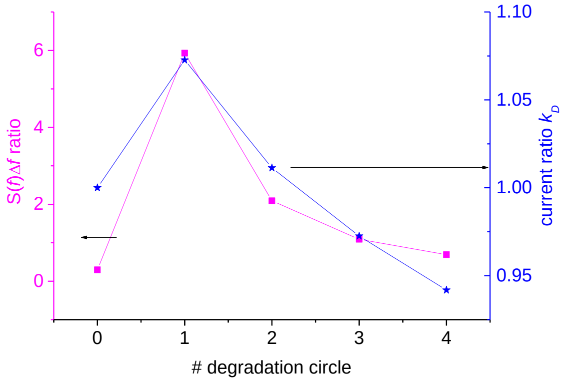

Figure 6. The ratio of maximum load currents k_D and the ratio of areas $\eta = S_{LF}/S_{HF}$ as functions of the number of fast degradation cycles.

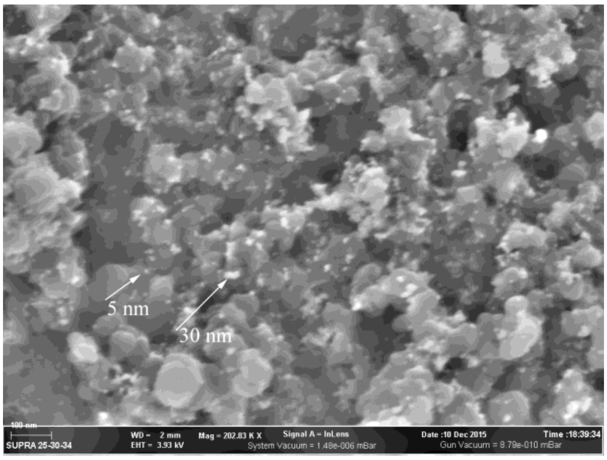

Figure 7. SEM images of the electrode surface with the catalyst. One can distinguish separate platinum particles with the size about 5 nm (light points) and agglomerates with a typical size of 30–40 nm.

Other parameters determined by FNS are summed up in Table 1.

Table 1. FNS parameters of the electrochemical noise of FC in the initial state and states realized after degradation treatment.

Degradation cycle n	Degradation degree k_{Dn}	FNS parameters					
		σ, μV	H_1	T_1, s	$S_c(T_0^{-1})$, (μV)^2·s	T_0, s	n_0
0	1	1.14	0.26	0.40	8.72	119	0.72
1	1.07	2.82	0.11	>> T	1.07	4.03	1.16
2	1.01	0.87	0.59	0.22	3.38	12.8	1.12
3	0.97	0.93	0.20	5.03	0.81	4.81	1.22
4	0.94	1.11	0.23	7.24	2.77	12.1	1.23

The parameters σ, H_1 is introduced in the expression (4), and $S_c(T_0^{-1})$, T_0, n_0 in the expression (5), degradation degree k_{Dn} is explained in (8).

The character of the change in chaotic components of the power spectrum and difference moment of the 2nd order can also point to the discussed structure changes that take place in the electrode. In particular, a change in spikiness parameter is a demonstrative one. The value of this parameter for the initial (nonactivated) catalytic electrode was $S_c(T_{01}^{-1})$ = 772 (μV)^2·s, and after first «degradation» step resulted in catalyst activation $S_c(T_{01}^{-1})$ decreased to 95 (μV)^2·s. The $S_c(T_{01}^{-1})$ is the parameter which characterizes a dynamics of the most important random variations in the chaotic component of measured potential. Such a decrease in it corresponds to a noticeable change in the structure of platinum cathode catalyst and can point to the increase in the active platinum surface in comparison with the initial one resulted from chemical deposition of the catalyst. However, in a macroscopic sense, these changes are not considerable since the analysis of corresponding SEM images does not reveal any visible changes. In the course of analysis of the PEMFC noise, the fact of structural changes in cathode catalyst is proved by the decrease in Hurst constant observed after the first degradation cycle (Table 1). This constant characterizes a dynamics of relatively small variations in the noise signal, i.e. variations in its diffusion component [7]. The increase in the surface of catalyst nanoparticles is also confirmed by the growth of T_1 parameter which characterizes the relaxation time of such a diffusion process (in general, an anomalous diffusion is meant).

The character of revealed dynamics of random variations in measured potential of the system under investigation changes considerably after further degradation treatment. In the course of the investigation of chaotic dynamics, these changes become pronounced after several degradation cycles (2, 3, 4). For the system in the degraded state, there is a decrease in load currents (after the second cycle) and the intermittent evolution with relatively high surges is prevailed. This assumption is proved by FNS data presented in Table 1. Namely, the spikiness parameter $S_c(T_{01}^{-1})$ increases after activation on the first cycle, and higher values of relaxation time T_0 corresponds to such a regime in contrast to the diffusion one with relaxation time T_1.

In the literature, there are a few known attempts of PEMFC electrochemical noise analysis. The reason for this is the novelty of the method and the shortcomings of the existing equipment [2]. This study became possible owing to the creation by Elins Ltd noise meter with very low self-noise. However, the correct study of the electrochemical noise of a fuel cell, for example, [19] and batteries [20, 21] is nevertheless carried.

The authors [19] investigated the electrochemical noise of the fuel cell. However, they were limited to investigating the dependence of the stochastic noise components on the FC work mode and not on its degradation over time. The obtained results are very interesting, but they practically do not overlap with our data. The fact that in this study analyzed only chaotic components of noise power, at high frequencies, not in the flicker-noise region. In addition the sensitivity of the apparatus used in [19] is not sufficient at high frequency (see. Fig. 3 of discussed article). Hence there is not analyzed noise caused by degradation processes in this work, but only the fluctuations of the main electrochemical reaction.

Similar measurements were made in [20], whose authors also performed measurements only at frequencies above 0.1 Hz, and also analyzed only chaotic component, with only n_0 parameter (in the notation of this article). The depending on the humidity measured in this article as well as our results show that in this case, the operation processes are analyzed, but not a degradation. For example, in our results n_0 increases after the first activation, and then remains constant.

We also believe that our method of approximation chaotic components is more informative. So, we found some relation between characteristic peaks as we guess due to the usage of more precise and specialized instrument with low self-noise. Because we used more long time data records, it made it possibly to analyze low-frequency part of the spectrum more clearly and to calculate correlation parameters more precisely.

In the papers 21 and 22, on the other hand, there was measured a FC noise and analyzed the characteristic frequency peaks in it's spectrum, but in the high-frequency region. Moreover, these authors did not use a Fourier analysis but a wavelet transform. And in the 22, is similar to ours, the change of the noise statistical parameters, such as degree of noise irregularities was calculated. So, in this paper is shown, that the Holder exponent (aka local Hurst exponent, H1) is not very sensitive to changes in the stoichiometry, but increases with a decrease in hydrogen pressure.

Unlike us, except analysis method, in [21, 22] there is investigated the change of noise parameters when changing modes of FC (feed gas stoichiometry and pressure) but no degradation in the fuel cell itself.

In work [23] was used a very short frequency range if we compare it with the frequency range we used. In this work, it was limited by 3 hertz at the low frequency to analyze electrochemical power source. In our work, the most interesting results were obtained in the frequencies lower than 1 hertz, and it would be impossible to obtain the slope of the power spectrums and Hurst constant if it would be limited for example by 1 hertz or 0.1 hertz.

Comparing to the work [24] we used more precise, and specialized instrument and our methods of calculations were more sophisticated and more phenomenological. We analyzed not an amplitude or standard deviation of noise changing during electrochemical power source degradation, but it's frequency dependencies which we guess has a more close connection with processes taking place in electrochemical power source during its degradation. Although comparing to works [19, 24] we used a measurement at open circuit potential without a long time loading a fuel cell because analyzing it this way we guess would be easier under an industrial condition where electrochemical power source would be used in real life and needed to be validated and analyzed using electrochemical noise techniques.

4. CONCLUSIONS

The task of the present study was to establish the possibilities of application of noise analysis in «equilibrium» conditions of potential drift fixation in order to reveal early degradation changes that take place in fuel cell electrodes, first of all in the anode. To extract a noise component from the time dependence of slow FC potential drift the Savitzky-Golay filter was used. This filter does not result in additional artifacts in contrast to approximation with polynomials of a high order. The noise resulted from this procedure was efficiently analyzed with flicker noise spectroscopy method.

The ratio of integrals of corresponding low- and high-frequency peaks in the noise power spectrum was shown to be an indicator of FC degradation degree.

At the same time, the first cycle of fast FC degradation (repeated polarization toward high potentials) results in an increase in catalytic activity of the electrodes and in corresponding FC load currents. Such an activation of electrodes can be assigned to the structural changes in the «catalytic platinum particles/carbon support/ionomer» system. The ratio of peak areas confirms this effect. However, other flicker noise characteristics such as Hurst constant which corresponds to the dynamics of random variations with a relatively small magnitude or spikiness factor (corresponds to high amplitude pulses) appeared to be sensitive exclusively to the electrode activation and a lesser degree to its degradation.

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