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Electrochemical noise analysis of a PEM fuel cell stack under long-time operation: noise signature in the frequency domain

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This paper is dedicated to the 65th birthday of Professor Fritz Scholz. The authors are very thankful to Professor Fritz Scholz, founder, and Editor-In-Chief of the Journal of Solid State Electrochemistry, for the interest and support of electrochemical noise diagnostics.

Abstract

Electrochemical noise (EN) generated by a PEM fuel cell stack (600 W, 8 cells with surface area 220 cm²) has been measured in well-controlled operational conditions following DOE recommendations for 100 h. For the first time, robust and stable statistical noise descriptors of a PEM fuel cell stack have been obtained based on PSD (power spectral density) spectra in the frequency range of 0.1 Hz < f < 10³ Hz. The reference noise signature of the stack involves white noise at the low-frequency range ($f < 0.1$ Hz), two fractional noises ($1/f^\alpha$) with different slopes, and a pronounced peak at the characteristic frequency $f = 1.6$ Hz. In the intermediate frequency range (0.1 Hz < f < 1 Hz) the slope $\alpha_1 = 1.49$ and in the high frequency range ($f > 10$ Hz) the slope $\alpha_2 = 3.23$. Qualitative interpretations of the obtained noise signature have been proposed.

The influence of interruption of stack operation on noise signature has been studied. It was shown that, just after a few hours, other peaks are visible in noise signature at $f = 0.004$ Hz and $f = 0.06$ Hz. These peaks disappear after about 20 h, this time can be considered as a characteristic time of relaxation of the slowest processes. It can be also noted, that during stack relaxation the slope in the intermediate frequency range increases and the slope at high-frequency domain remains constant. It seems that fractional noise at high-frequency range reflects charge transfer processes in catalytic layers with smaller time constants. On the other hand, low and intermediate frequency ranges are related to mass transport and water management processes with higher time constants.

Keywords. Electrochemical noise, Statistical descriptors, PEM fuel cell stack, Relaxation processes, Aging experiments

1. Introduction

In a world where the energy demand increases irremediably, where the forthcoming shortage of fossil fuels is in front of us and the pollution issues related to them are discernible, the science and industry are strongly motivated to explore alternatives. In the area of hydrogen technology, fuel cell systems have emerged as a sustainable alternative for decentralized electricity production, with high-energy efficiency and low/zero green gas emissions [1-3]. Hydrogen is not a primary energy source but a vector. To be clean, fuel cell systems must use hydrogen production with a lower environmental impact as possible [4]. Unfortunately, hydrogen is mostly produced with fossil fuels (96%), so environmental problems are not solved. But hydrogen production becomes relevant if renewable energy (solar, wind, biomass) is used.

Indeed, this vector solves the intermittence and/or variability problem of renewable energy. It allows for massive storage of energy for several weeks or months. In the field of green chemistry, hydrogen can be seen as a byproduct of the bio-electrochemical conversion of organic compounds [5-7]. Microbial Fuel Cells [8, 9] can be relevant to obtain the sustainable conversion of energy. More generally, electrochemical reactor development in water or chemical treatment [10, 11] is a topic of interest.

Proton Exchange Membrane Fuel Cell (PEMFC) technology is a promising system due to its advantages such as low-temperature range operation 60 – 90°C, high efficiency (up to 70%) in cogeneration of heat and electricity for residential applications [12], and its reasonable efficiency for transport applications (30 at 60% depending on operating point). Fuel cells have a high-power density, quick start-up, low weight, and quietness [13]. Unfortunately, some drawbacks are not overcome, such as high cost, catalyst degradation, complex water management, insufficient reliability, and durability [14]. Numerous studies have been done concerning fabrication optimization [15-17], catalyst modification [18], understanding of water, and thermal management [19, 20]. Nevertheless, all the disadvantages are not still eliminated, which impede a wide utilization and commercialization of PEMFC.

To improve the performance and the durability of the PEMFC, different diagnostics tools and methods are used like impedance spectroscopy, current interruption technique, temperature distribution measurements, aging test protocols, optical imaging, x-ray tomography. But the development of reliable diagnostics tools applicable without operation interruption is still an open problem. One of the promising possibilities allowing in-situ diagnosis of electrochemical energy sources, without system perturbations, is related to electrochemical noise analysis (ENA) [21-23]. Indeed, electrochemical noise measurements

can provide statistical descriptors with the high sensibility to diagnose the behavior of an electrochemical system without any interruption.

Electrochemical noise (EN) is defined as a spontaneous fluctuations of potential and/or current generated by electrochemical processes [23, 24] due to different phenomena such as turbulent mass transfer [25–27], gas evolution [28, 29], electrode corrosion [30–32], passivation [33], water transport and transfers within fuel cells [19, 34, 35]. In the last decades, ENA was also developed to study battery systems [36–38] and coating processes [39, 40]. The goal of ENA is to produce statistical descriptors in time (moments) or frequency (spectra) domains. Time-frequency analysis (wavelets) is also used, nevertheless, it is more difficult for practical applications. Signals originating from PEM fuel cells, battery systems, and corrosion processes are often non-stationary because of the presence of a significant DC drift [41, 42]. So, adapted pre-processing methods are necessary to detrend correctly the drift of the signal [43, 44].

Despite the numerous advantages, ENA is a relatively new experimental method and a lot of efforts are still necessary to introduce it for everyday electrochemical studies. These efforts concern the development of user-friendliness instrumentation, experimental procedures to obtain robust statistical descriptors and theoretical approaches for interpretation ENA. One of the main advantages of ENA is the possibility of in-situ monitoring of electrochemical power sources during long-time operation, in particular concerning aging experiments. Information regarding ENA in these conditions is very scanty. Indeed, available literature on ENA concerns mainly single fuel cells during relatively short time operation (about one hour).

One of the goals of the present paper is the demonstration of the ENA applicability to monitoring a PEM fuel cell stack under long-time operation. In our knowledge, it is a first attempt to apply ENA for a relatively high power PEMFC stack. The noise measurements have been recorded for about 100h in the galvanostatic regime. Stack temperature, humidification, flow rate, and pressure of gases have been controlled precisely to avoid any significant drift of the mean voltage and assuming a constant electrical power generation by PEM fuel cell stack. The provided measurements have allowed us to obtain a highly representative database suitable for ENA methodology development.

The first question deals with ENA concerns the generation of robust statistical descriptors. In this paper, the attention is focused on statistical descriptors in the frequency domain, namely on power spectral density (PSD) of voltage fluctuations. It is necessary to note that PSD is the most usual tool for characterizing stochastic signals. Nevertheless, it is well known, that PSD estimation meets certain difficulties related to the methodology of calculations. The choice of operating parameters (data acquisition frequency and signal duration) and elimination of possible signal trend is also a critical point.

Disregarding these difficulties leads to ambiguities of PSD estimation. To obtain a robust estimation of PSD in a high-frequency range, it is necessary to have stationarity of the signal during a long-time period. The experimental campaign allows this possibility and special attention has been put for the justification of robustness of the obtained spectral descriptors (PSD). In this way, some reference noise signature of the PEM fuel cell stack has been obtained.

When a reference noise signature of the stack is available, this information can be used as a descriptor to characterize the state of the system. In this paper, the influence of the stack interruption on its characteristics has been studied. ENA has been used to determine the relaxation time necessary for the recovering of the stack. This result can be important for the methodology of aging experiments and prognostics of fuel cell stacks. Indeed, all traditional methods require interruption of the system, for example, polarization curve measurements, or at least some system perturbations, for example, impedance measurements.

The principal question concerns the physical interpretation of the obtained noise signature. Sure, it is not simple to develop a theoretical approach that supports noise measurements. Some attempts in this direction have been done concerning turbulent noise measurements [25, 45, 46], in the case when the source of fluctuations is well identified and some theoretical background, namely mass transport equation, is available. Concerning EN of fuel cells, the problem is still open and not very different from the one related to the interpretation of the impedance measurements. One of the main difficulties is determined by the general problem of a correct theoretical description of the electrochemical system. Existing theories reveal some partial phenomena and are not still able to give a complete description of the studied system. So, the interpretation of noise measurements should be developed progressively based on robust experimental information and independent cross-measurements. This is not a goal of the present study, the theoretical discussion of the obtained noise signature is restrictive here to some qualitative interpretations and working hypothesis. The main goal of the paper is the generation of robust statistical descriptors in the frequency domain which can be used as a reference for future studies.

The paper is organized in the following way. Section 2 presents the experimental details of the provided experiments. In section 3, the details related to the PSD estimation are presented and the robustness of obtained statistical descriptors is considered. The reference noise signature of the stack under operation is presented and discussed in section 4. Section 5 deals with the influence of the stack interruption on the noise signature. The discussion of obtained results and conclusions are given in the last section 6.

2. Experiments

The experiments have been provided using the PEM fuel cell stack of the nominal power 600 W fabricated by CEA (Commissariat à l'Energie Atomique), Grenoble, France. The principal schema of the stack is presented in Fig. 1.

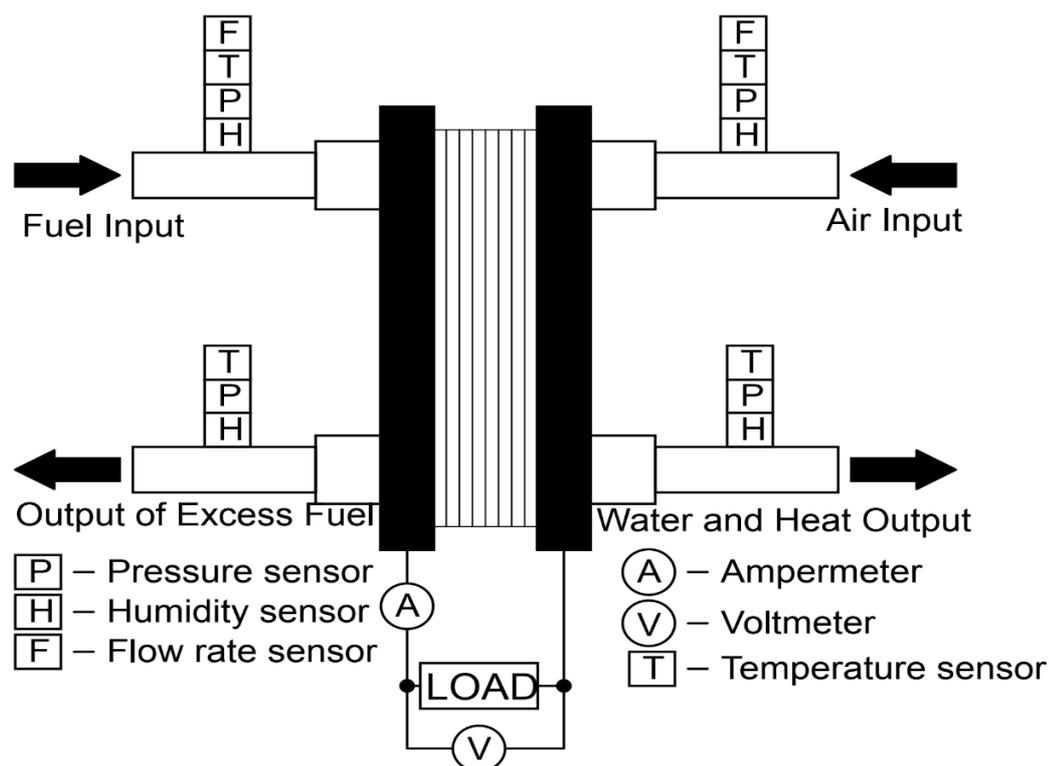


Fig. 1 Principal schema of PEM fuel cell stack using for electrochemical noise measurements

The stack has been assembled using 8 cells with a surface area of 220 cm². Each cell of the stack is composed of coated stainless steel flow field plates presenting multiserpentine geometry with a square section of 1mm x 1mm. An NRE 212 Nafion[®] Membrane Electrode Assembly (MEA) is sandwiched between 25 BC Sigracet[®] Porous Transports Layers (PTLs often named GDLs). The test bench has been equipped by sensors allowing temperature, pressure, humidity, and reactants flow rate measurements. The conception of the experiments was oriented to obtain a continuous long-time operation of the stack up to 1000h. Operational conditions meet DOE recommendations, namely 1.5 bar anode and cathode pressure, 75°C stack temperature, 50% anode, and cathode relative humidity, reagents H₂/air stoichiometry 1.5/2. Pressure regulators supported high-pressure stability. The accuracy of the temperature controller was higher than 0.2°C. The flow rate regulator error does not exceed 0.2%. Electrical operation modes of the stack have been controlled by the electronic load of TDI Dynaload

RBL488-400-600-4000. The additional noise provided by this module is significantly lower than 1 mV. A more detailed examination of the electronic load impact on EN measurements will be given below in section 4. Before the launch of the long-duration campaign (1000h), a polarization curve has been recorded for characterizing the electrical performance of the stack, see Fig. 2.

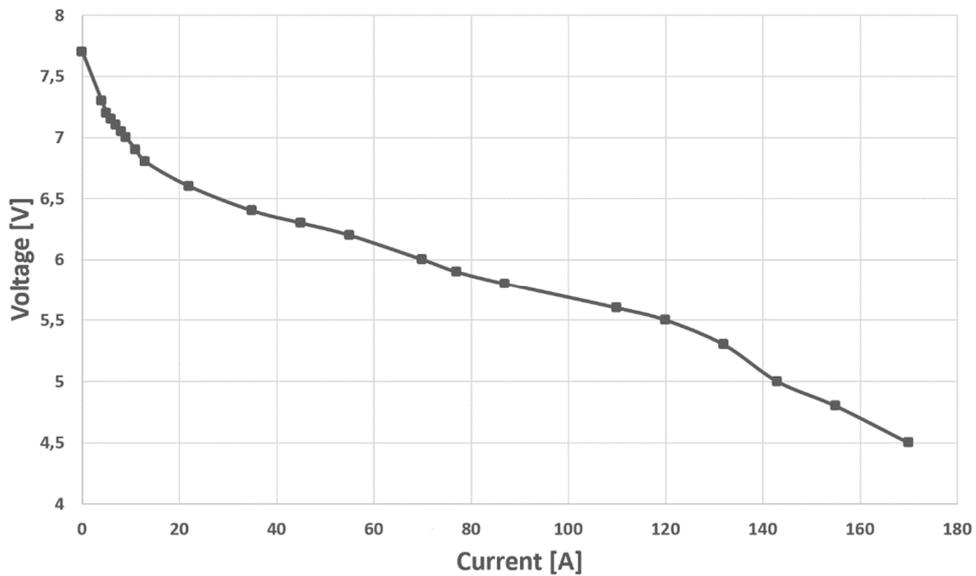


Fig. 2 Polarization curve of the fuel cell stack

The stack has been operated in galvanostatic mode and the current load was set at 85 A ($\sim 0.4\text{A}/\text{cm}^2$). The duration of electrochemical noise (EN) measurements was about 100h and cover only a part of the total experimental campaign, see Fig. 3. The noise measurements have started approximately at $t = 380$ h after the beginning of the experimental campaign, and have been interrupted because of the lack of fuel supply. The duration of these first measurements was about 10 h. The results are denominated as A_1^{85} . Short time measurements have been provided for comparison under open-circuit conditions (A_1^0). When the technical problem with the fuel supply has been solved, additional electrochemical noise measurements have been provided during 90 h in the same operational conditions (A_2^{85}). These measurements are subdivided on three zones $A_{2,1}^{85}$, $A_{2,2}^{85}$, $A_{2,3}^{85}$. The noise measurements have been interrupted with the experimental campaign because of the stack degradation.

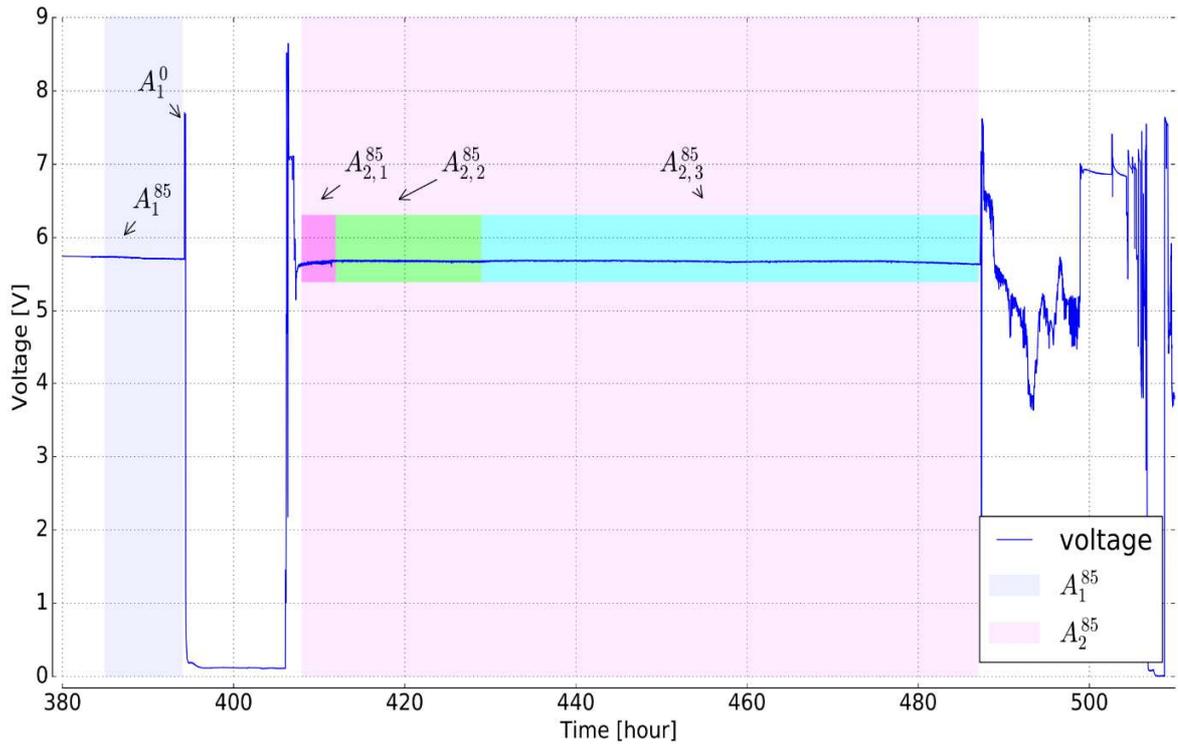


Fig. 3 Different zones where electrochemical noise measurements have been provided

The electrochemical noise measurements concern high-frequency recording of the stack voltage. A special system of data acquisition and storage have been developed for this purpose. The measurement system is based on a data acquisition card (DAQ) from National Instruments (NI-9239) with a sampling frequency of 50 kHz. The card is placed inside a metallic box for decreasing electromagnetic environmental influence and the wires are connected to output terminals of the stack. The intrinsic noise of the measuring system was about $70 \mu\text{V}$ (root mean square value under short-circuit connection). This value of intrinsic noise allows correct measurements of stack voltage fluctuations (electrochemical noise) which are of mV-order magnitude.

LabVIEW[®] software from National Instruments was used for DAQ configuration as well as data pre-storage. Additional functions have been performed by developed software on Python 3. All data from DAQ were automatically compressed and saved within the corresponding folder for the following transfer to the external hard drive. Storage and data management have been performed by using a laptop. The developed system allows simultaneous 4 channels measurements and data storage with the sampling frequency up to 50 kHz. However, the frequency of 2 kHz is sufficient for the provided experiments and all results presented below have been obtained with this sampling frequency. The possibility of in-situ data storage is very important. Indeed, the recorded voltage fluctuations present some stochastic signals

which can be treated in different ways. In the present paper, the most classical approach based on power spectral density (PSD) calculations are used. More sophisticated treatment of the recorded stochastic signals is under development.

Examples of the recorded electrochemical noise signals are presented in Fig. 4. The origin for each signal has been arbitrarily selected to place all these signals in the same figure. The stochastic character of the recorded signals can be seen with some dominant frequencies existence. It is also possible to estimate the amplitude of the fluctuations which is about 10 mV. It confirms that the developed acquisition system with an intrinsic apparatus noise of 70 μV is well adapted for this type of measurements.

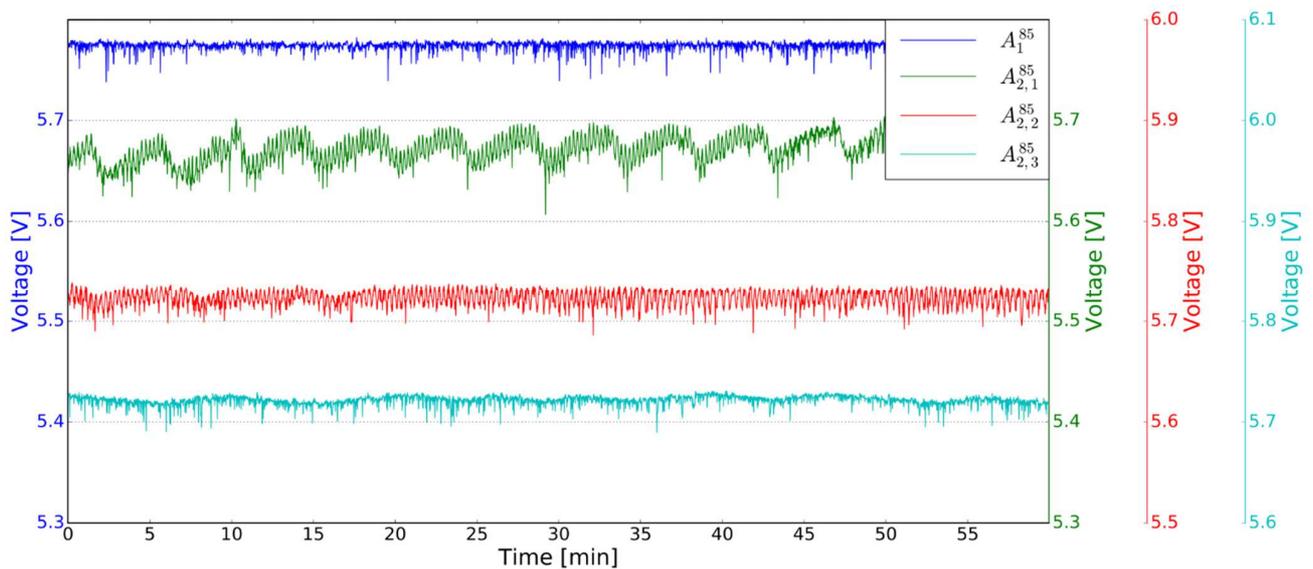


Fig. 4 Electrochemical noise signals recorded in different zones

3. Robustness of spectral descriptors

Once the electrochemical noise signal is recorded and storage the question of data treatment arises. Indeed, the goal of the noise measurements is the generation of some statistical descriptors which can be used for the characterization of the studied electrochemical system. The first principal difficulty which one meets in this way is related to the definition of the signal fluctuations. In other words, with the definition of the noise notion. It seems to be simple: the fluctuations (the noise) are the difference between the raw signal and the mean signal values. But what is the mean value of the signal? When the process is stationary this value can be calculated as the mean value for the total signal duration or some representative part of the signal realization. Nevertheless, in reality, it is never known either the process is non stationary or it can be treated as a stationary one. Thus, different procedures of signal detrending

are used, as apparatus filtering. When the actual signal data are stored, the detrending can be implemented numerically. The goal of the detrending procedure is the elimination of the mean signal value. All these procedures influence the noise. The advantage of numerical detrending deals with the possibility to control this influence. Contrary, it is difficult to provide the same level of control with analog filters due to the influences of parameter spread, thermal effects, etc.

In the present study, the raw signal values were recorded and stored. Thus, numerical detrending was possible and has been used. The total signal is divided into windows and the values of the mean signal is calculated within these windows, using the 5-order polynomial fitting. The length of the window varied from 0.3 s to 32 s. Varying the length of the window makes possible estimation of the influence of the detrending procedure on noise characteristics. More precisely, the window acts as a filter and the length of the window determines the filter characteristics. Fig. 5 presents an example of the provided numerical detrending. The origin value for each signal has been selected arbitrarily to place all the signals on the same figure. Decreasing the size of the windows, from 32 s to 0,3 s reduce the noise intensity. This effect can be explained by low frequencies cut-off.

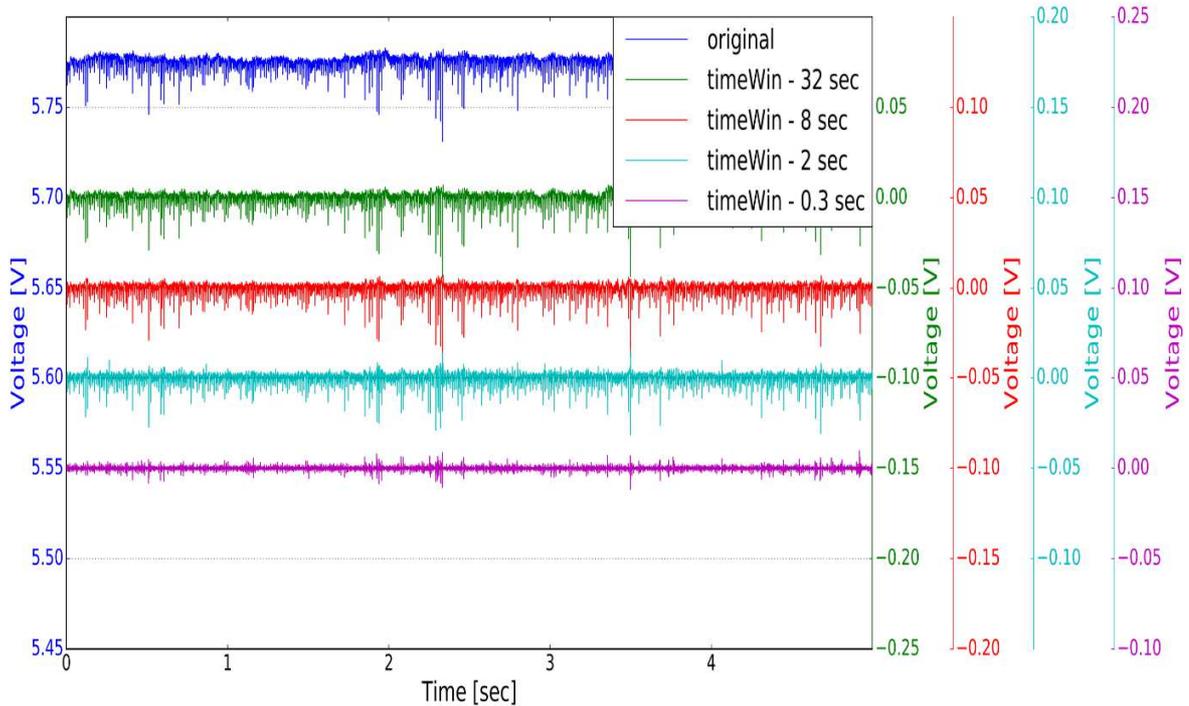


Fig. 5 Detrending of original electrochemical noise signal

In the present paper, the classical approach for stochastic signals treatment in the frequency domain is used. This approach is based on the calculation of power spectral density (PSD). There are numerous methods for PSD calculations and these methods influence PSD estimation. It is not a goal of the present study to discuss all problems related to the spectral analysis. In this paper, the influence of the signal duration T , and the method of calculations (Welch or Burg) have been studied. The influence of the numerical detrending on PSD is discussed in section 4. Both Burg and Welch methods are used for PSD estimations [47]. Burg is a parametric autoregressive method. The estimation of PSD is based on the parametric model of the random process and the minimizing of the forward and backward prediction errors. Welch method uses periodograms and provides spectrum estimation using overlapping windowed experimental data segments. The results presented in Figs. 6 - 7 have been obtained with the original (non-detrending) signal recorded in the zone A_1 ⁸⁵.

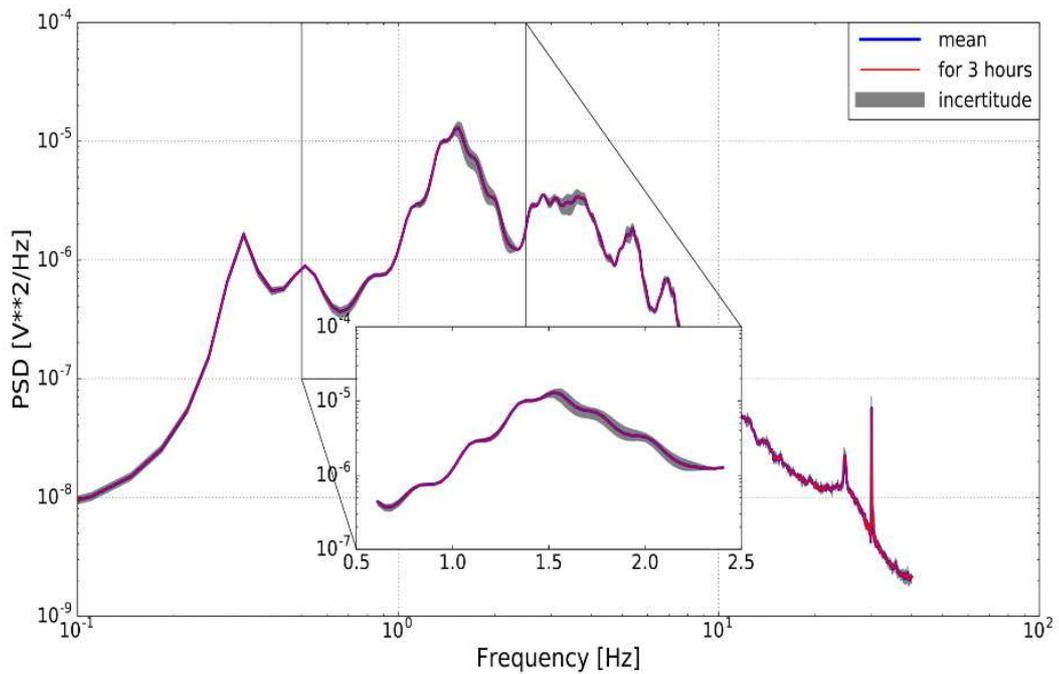


Fig. 6a PSD of original electrochemical noise signal calculated by Burg method

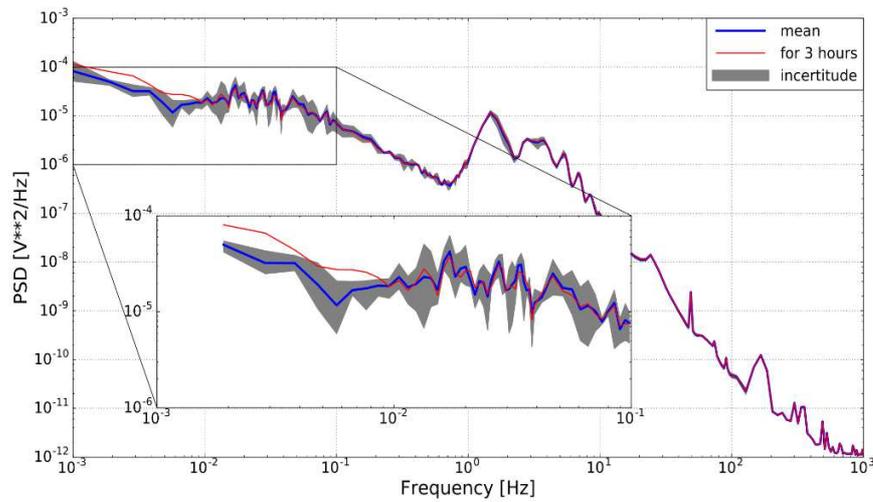


Fig. 6b PSD of original electrochemical noise signal calculated by Welch method

Firstly, PSD is calculated for a signal duration of 1 h. Then, three calculated PSD spectra are used for the calculation of the mean PSD and the estimation of its confidence. Next, PSD has been calculated for the signal duration of 3 h (Fig. 6a, b). Results show that for 3 h estimation, the PSD is situated mainly within the confidence band. Thus, the duration of 1h seems to be sufficient for a correct PSD estimation within the frame of provided experiments.

This conclusion is supported by Fig. 6c which presents the calculation of PSD by Welch method for 1h, 3h, and 9h signal duration. A comparison between Burg and Welch methods is given in Fig. 7. Results show a similar PSD estimation in the main frequency range. Only at a very-low-frequency range (less than 0.1 Hz), the estimation of PSD highlights some differences. These differences are not discussed here. It can be concluded that a robust estimation of PSD for studied signals in the frequency range $f > 0.1$ Hz can be obtained using the Welch method with 1h signal duration. The use of the Welch method is justified by a lower calculation cost.

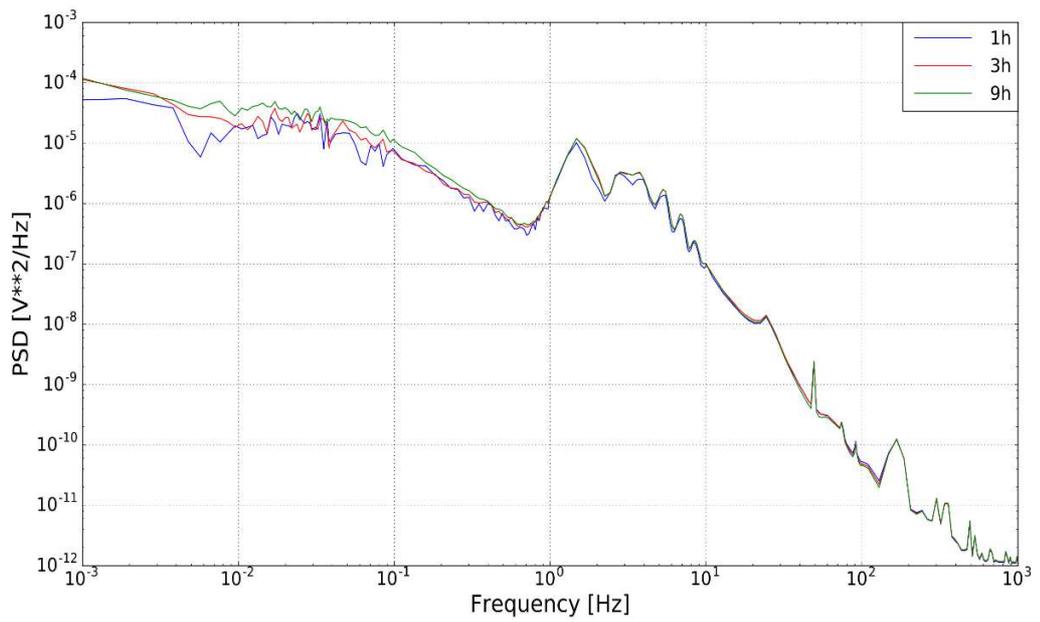


Fig. 6c PSD calculated by Welch method for different signal durations T = 1h, 3h, 9h.

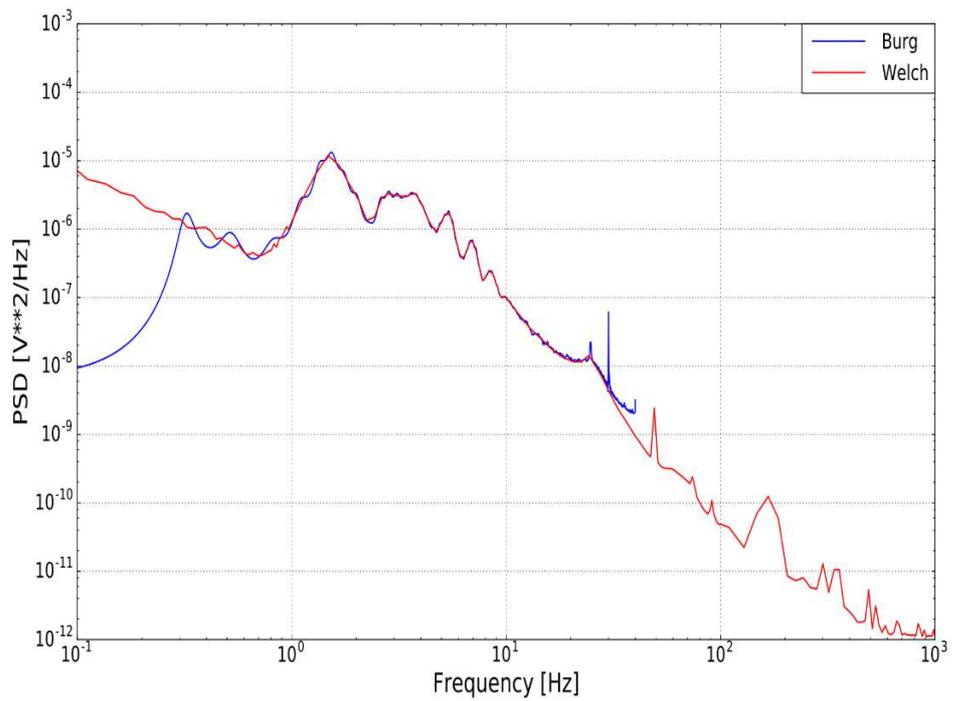


Fig. 7 Comparison between Burg and Welch methods for signal duration T = 3h.

4. Noise signature of the stack in the frequency domain

Once the data treatment parameters allowing robust estimation of PSD are determined ($T = 1\text{h}$, Welch method), these spectra can be interpreted as statistical descriptors of the studied PEMFC stack. Fig. 8 presents the PSD spectra calculated for the A_1^{85} zone. The noise measurements have been provided before the interruption of the stack under operation. This spectral descriptor can be interpreted as a reference noise signature of the studied stack in normal operational conditions.

PSD spectra calculations presented in Fig. 8 come from the original signal and signals after detrending using different time windows. The influence of the detrending procedure is rather clear. The window acts as a filter with specific cut-off frequency. Large-time windows allow us to obtain PSD spectra in a lower frequency range. On the other hand, short-time windows can be interesting for the high-frequency range when the system parameters change rapidly. It can be noted a certain influence of the size of the time window on PSD estimation in a high-frequency range. In all the cases, the choice of data treatment parameters influences PSD spectra and the researcher should pay attention to this point. In our case, the problem of signal detrending has been successfully solved employing polynomial fitting of the mean signal value within the window. It was demonstrated that the order of polynomial fitting has no high influence on PSD spectra. The impact of a polynomial fitting up to the 7th order has been studied.

The obtained noise signature is complex and very different from flicker-noise ($1/f$). This noise is usually founded in electronic devices. It cannot be reduced also to pink noise ($1/f^\alpha$ with $0 < \alpha < 2$) which occurs widely in nature. Here, f stands to the frequency of signal fluctuations. Using proposed by Mandelbrot terminology, the noise signature of the stack can be described as a combination of different fractional (fractal) noises with $f^{-\alpha}$ behavior where the value of power factor α can higher than 2.

The obtained noise signature of the stack involves:

- white noise in low frequency range ($f < 0.1\text{ Hz}$)
- first fractional noise with the slop $\alpha_1 = 1.49$ at intermediate frequency range ($0.1\text{ Hz} < f < 1\text{ Hz}$)
- pronounced peak at $f = 1.6\text{ Hz}$
- second fractional noise with the slop $\alpha_2 = 3.23$ at high frequency range ($f > 10\text{ Hz}$)

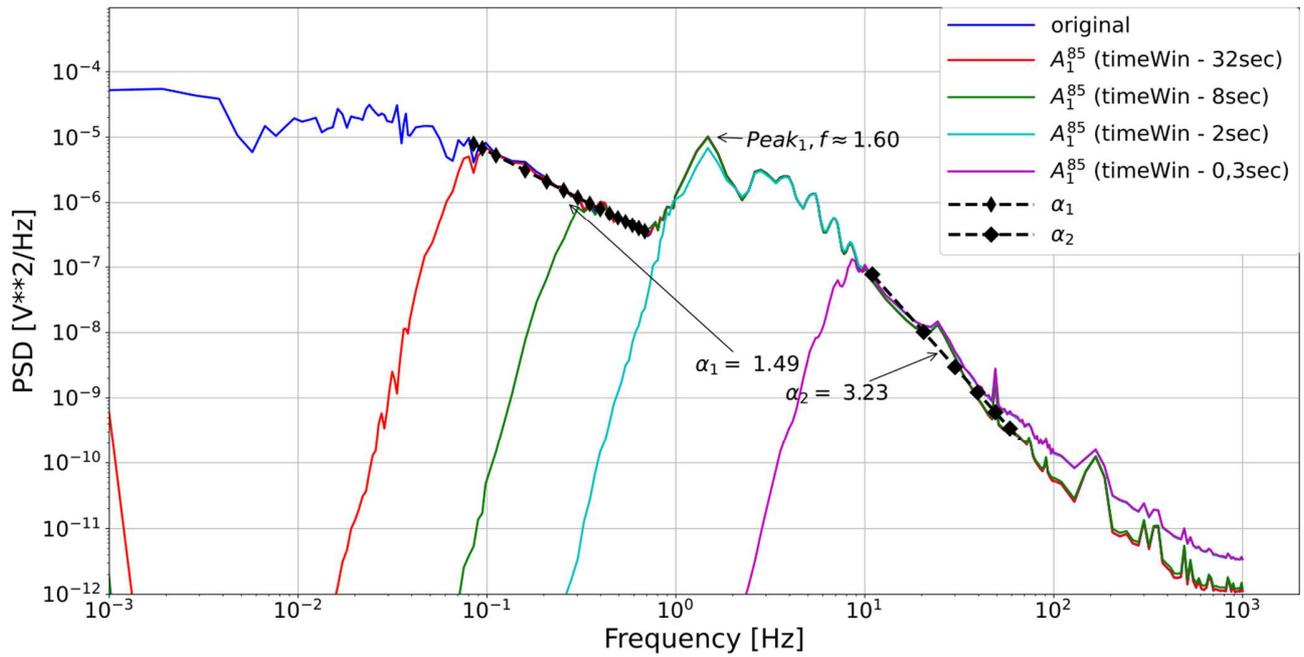


Fig. 8 PSD spectra for A_1^{85} zone calculated for original and detrending signal

The existence of fractional noise with $\alpha > 2$ reflects the complex character of physicochemical processes in electrochemical systems, in particular related to mass transport. For example, theoretical studies of turbulent noise in electrochemical systems [25] show, that for a fully developed diffusion layer, turbulent fluctuations of the limiting diffusion current highlight a fractional noise with $\alpha = 3$. This result has been obtained supposing that the source of electrochemical noise, namely the velocity fluctuations (hydrodynamic noise), is white noise in the studied frequency range. The reason for these fractional noise behavior ($\alpha = 3$) is due to the attenuation of hydrodynamic fluctuations through the diffusion layer which acts as a filter. It was shown that a more complex character of the hydrodynamic noise (for example fractional behavior) manifests itself in the further increase of the power factor α for fractional electrochemical noise, thus $\alpha > 3$. A more detailed discussion of the theory of turbulent noise in electrochemical systems and additional references can be found in a recent publication [46]. In particular, it was demonstrated the dependence of power factor α on the electrode geometry. It was shown that kinetics of electrochemical reaction influences also the turbulent noise behavior and leads to increasing of power factor $\alpha > 3$. Some details including experimental verifications are available in the literature [26, 27, 45]. So, the obtained noise signature of the fuel cell stack is not surprising for electrochemical systems and theoretical approaches developed for an explanation of the turbulent electrochemical noise can be useful for ENA as well.

The recorded noise signature of the stack allows us to propose a more detailed estimation of the

influence of intrinsic apparatus noise, in particular the load, on ENA. Fig. 8 shows that PSD in the high-frequency region (about 1 kHz) has a value of about 10^{-12} V²/Hz. It is possible to consider this noise level as an upper estimation of inherent electronic noises of measurement and control devices (DAQ, electronic load, etc.) for a given frequency. Supposing that the apparatus noise has a traditional flicker nature ($1/f$), the level of apparatus noise for other frequency ranges can be estimated. For example, at $f = 100$ Hz the upper estimation of apparatus noise gives 10^{-11} V²/Hz. The proposed estimation justifies that apparatus noise is negligible in the frame of provided ENA.

5. Stack characteristics recovering after interruption of its operation

Despite the limited theoretical background for noise measurement interpretation, ENA can be used for the direct characterization of electrochemical systems empirically. For this purpose, the noise signature of the operating electrochemical system should be compared with its reference value. In this section, this approach is used to study the stack behavior after interruption of its operation.

Fig. 9-11 present PSD spectra for $A_{2,1}^{85}$, $A_{2,2}^{85}$, $A_{2,3}^{85}$ zones. The noise measurements have been provided with the same stack and in the same operational conditions as for the A_1^{85} zone. The noise signature for all these zones is similar to the one obtained for the zone A_1^{85} . In particular, two fractional noises with the slopes α_1 , α_2 and a pronounced peak at $f = 1.6$ Hz can be seen in the frequency range $f > 0.1$ Hz.

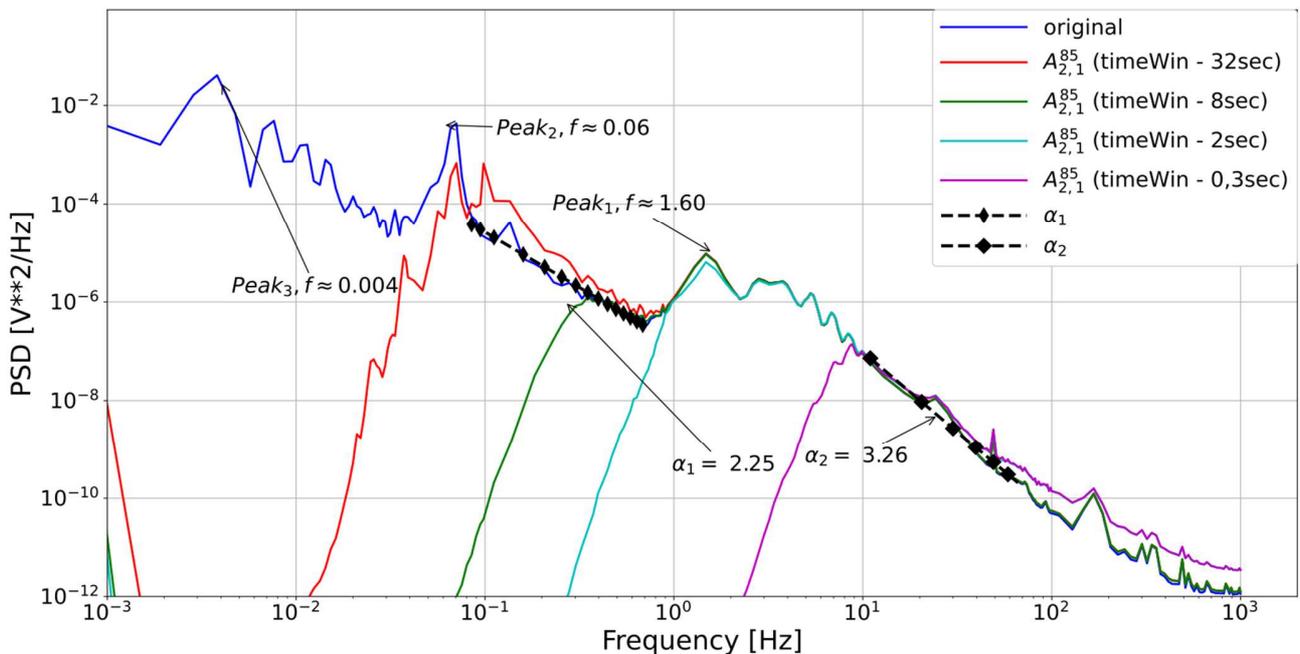


Fig. 9 PSD spectra for $A_{2,1}^{85}$ zone calculated for original and detrending signal

In more detail, PSD spectra for the zones $A_{2,1}^{85}$, $A_{2,2}^{85}$ are slightly different from the one obtained for the zone A_1^{85} . Indeed, in these zones for the low-frequency range $f < 0.1$ Hz, other peaks are visible at $f = 0.004$ Hz and $f = 0.06$ Hz. On the other hand, these peaks disappear in the zone $A_{2,3}^{85}$. In our opinion, the existence of the other peaks reflects the transitional processes in the stack after interruption of its operation. Thus, ENA allows us to determine the relaxation time (in our case about 20 h) which is necessary for complete stabilization of stack characteristics after a sudden interruption. It can be noted also, that during stack relaxation the slope α_1 in the intermediate frequency range increases from 2 to 2.5, while the slope α_2 in the high-frequency domain remains constant. The obtained noise signature reflects different processes that take place in the stack under operation. Naturally, different phenomena have different relaxation times. Fractional noise at high-frequency range reflects processes with small time constants. It can be due to charge transfer processes in catalytic layers. On the other hand, low and intermediate frequency ranges are related to more important time constants. These can be related to mass transport and water management processes. At the last, good stability of the characteristic peak at $f = 1.6$ Hz is noted.

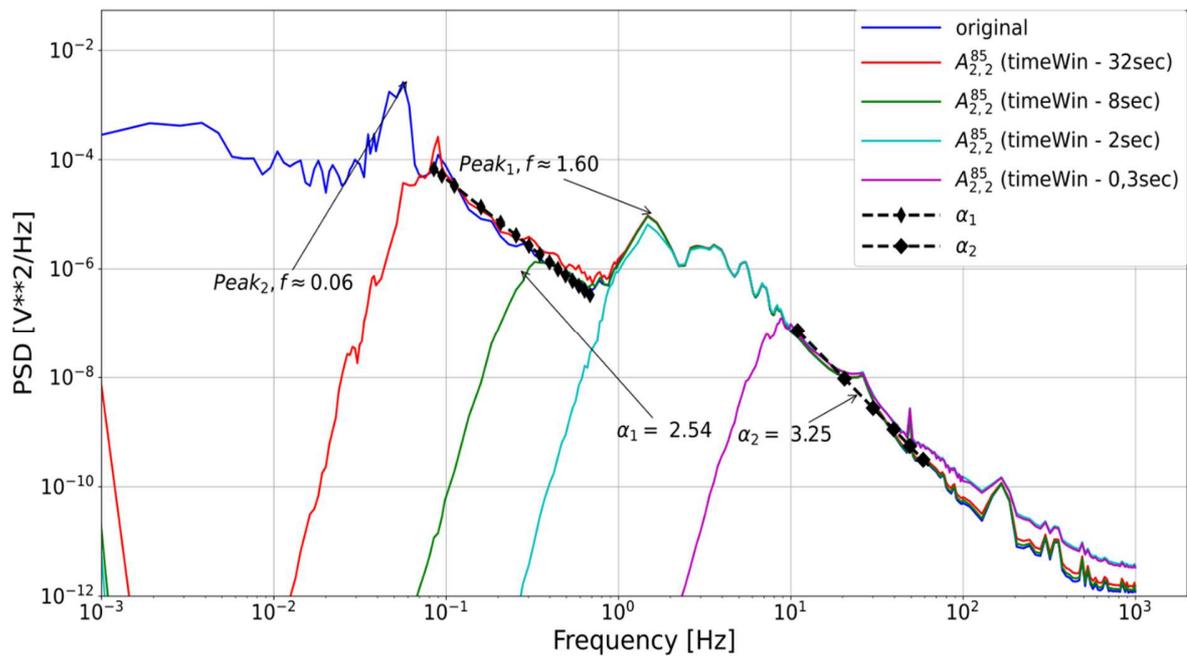


Fig. 10 PSD spectra for $A_{2,2}^{85}$ zone calculated for original and detrending signal

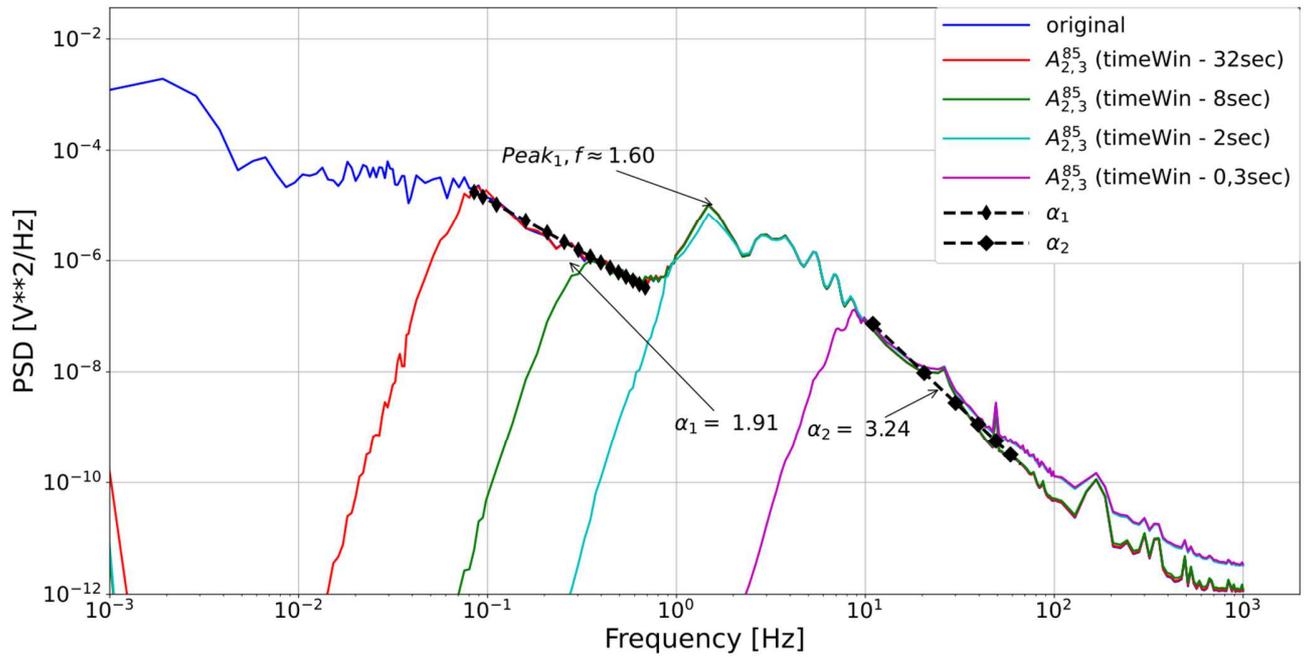


Fig. 11 PSD spectra for $A_{2,3}^{85}$ zone calculated for original and detrending signal

6. Discussion and Conclusions

In our knowledge, this is the first time when ENA was applied for PEMFC stack. The robust noise signature (PSD) of the stack has been obtained in a large frequency range ($0.1 \text{ Hz} < f < 1 \text{ kHz}$) using long-time electrochemical noise (EN) measurements. A large representative database of noise measurements has been acquired during a long duration campaign (about 100 h) with well-controlled experimental conditions. Thanks to this database, the robustness of the stack noise signature in the studied frequency domain has been confirmed. Namely, the influence of signal duration, data treatment, and detrending procedure on PSD estimation has been investigated.

The obtained noise signature includes white noise in a low-frequency range, two fractional noises ($1/f^\alpha$) with different slopes, and a pronounced peak at $f = 1.6 \text{ Hz}$. While in nature a pink noise ($0 < \alpha < 2$) is widely presented, a fractional noise with a slope $\alpha \approx 3.25$ has been founded in stack noise signature. In our opinion, this noise reflects specific physicochemical phenomena in electrochemical systems. It can be noted, that fractional noise with a slope $\alpha > 2$ has been founded in electrochemical turbulent noise studies also [26, 27, 45]. Theoretical studies [25, 46] demonstrate that high values of the slope α in electrochemical turbulent noise signature are related to attenuation of hydrodynamic fluctuations through the diffusion layer which acts as a filter. For the most principal case of the fully developed diffusion

layer, the turbulent noise of the limiting diffusion current reveals $\alpha = 3$ behavior [25, 46]. This result has been obtained supposing that the primary source of the electrochemical noise, namely the velocity fluctuations (hydrodynamic noise), is white noise in the studied frequency range. It was shown that kinetics of electrochemical reaction also influences the turbulent noise behavior and leads to increasing of power factor $\alpha > 3$, additional references can be found in [46].

Actual information on the ENA of fuel cell systems concerns mainly single cells during relatively short time operation [22, 23, 35]. Experiments in these conditions meet well-known difficulties related to the interpretation of PSD spectra. Indeed, the robustness of PSD estimations depends on accessible statistical information and is very sensitive to the data treatment procedure. The main possibility to increase statistical information is related to the long duration experiments in well-controlled conditions as provided in this study. Moreover, statistical information is proportional to the scale of the studied system, namely to the total active surface area of MEA (in our experiments 220 cm²). Previous works [22, 23, 35] reported experiments concerning single cells with a 1 cm² surface area. That is why stack noise experiments are much more representative, from the statistical point of view, in comparison to the experiments with small single cells.

The results presented in the literature [22, 23, 35] show that EN of single cells is fractional ($1 / f^\alpha$) and reported different values for the slope α . For example, a fractional noise with $\alpha = 2$, both in high ($f > 3$ Hz) and low ($f < 0.3$ Hz) frequency range has been reported in [35], with a more or less pronounced plateau between these zones. Qualitatively the same results are reported by the same author [22], where PSD calculations were rectified using wavelets. On the other hand, high values of $\alpha = 2.5 - 3$ are reported in [23]. Our previous studies with single cells [34, 48] also indicate the existence of fractional noises with different slopes depending on frequency range and operational conditions. Identification of these slopes undoubtedly depends on the data treatment procedure that is why it is difficult to provide a quantitative comparison. Nevertheless, some conclusions can be done. It seems a pink noise with $\alpha = 2$ in the low-frequency range can be related to transients in the recorded signals. The tentative to extrapolate PSD calculations on low-frequency range requires the decreasing of number of windows in experimental segmented data. In this case, transients manifest themselves like pronounced pink noise with $\alpha = 2$. It can be noted also that Brownian motion highlights a pink noise with $\alpha = 2$. In our previous work with a single cell [48], it was shown that PSD in the low and intermediate frequency range is extremely sensitive to fuel cell water management. The change of reactant humidification can modify drastically the shape of PSD spectra and different fractional noises have been detected, in particular with $\alpha > 2$. No significant peaks have been reported in the above-cited papers related to the ENA of single cells.

Currently, there is no theory of EN in electrochemical sources of energy. Sure, it is not simple to

develop a theoretical approach supported noise measurements and this problem is still open. So, below only some qualitative explanations are presented which should be considered as a working hypothesis. It seems that noise signature in the low-frequency range ($f < 10$ Hz) is mainly influenced by water management (mass transport and membrane humidification). This is supported by our previous experiments in a single cell with a variation of humidity conditions [48]. Impedance measurements confirm also that the low-frequency range is mainly influenced by transport phenomena. Indeed, mass transport phenomena have important characteristic times, so all non-stationary methods should be sensitive to these phenomena in a low-frequency range. Accepting that low-frequency noise reflects mass transport and humidification phenomena, it is reasonable to suppose that characteristic peak at $f = 1.6$ Hz has the same physical nature. One of the possible explanations is related to the process of liquid droplets rising and evacuation. Sure, it is necessary to provide cross-measurements between voltage electrochemical noise and pressure and flows rate signals. These cross-measurements have been already down in our previous work with a single cell [21] where statistical descriptors were calculated in the time domain.

In the high frequency range ($f > 10$ Hz), a fractional noise slope $\alpha = 3.25$ is detected. The stability of this parameter is highlighted. The independence of this slope value from relaxation processes after stack interruption has been demonstrated. Fractional noise with $\alpha > 2$ is not typical and can be attributed to charge transfer processes in catalytic layers (triple-phase boundary). This hypothesis is also supported by analogy with the impedance measurements. Sure, all these hypotheses should be verified in future experiments allowing regulation of working parameters and cross-measurements using other sensors.

In conclusion, noise measurements allow a non-destructive in-situ diagnostics of electrochemical sources of energy without any perturbation of system operation. Further experimental studies, as cross concomitant signals measurements, and the production of a high informative database thanks to a comparison between several operating conditions and systems will help to develop noise theory. Statistical descriptors in the frequency domain (PSD) reflect phenomena with different characteristic times. The noise signature of the PEMFC stack is highly informative, extremely sensitive but not simple to interpret. Nevertheless, ENA can be used directly in an empirical manner using a comparison of the in-operando noise signature of the system with its reference value. In the present study, this approach has been used to explore relaxation processes within the stack after a sudden interruption of its operation. Development of ENA and its implementation in everyday electrochemical studies necessitate important experimental efforts and the development of suitable theoretical approaches. These approaches should be developed progressively based on strong experimental information. Long duration noise measurements in-operando stack have been provided for the first time and a robust noise signature of

this electrochemical system has been obtained. This signature is suitable for further development of the ENA methodology.

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8. References

- [1] Dicks AL, Rand DAJ (2018) Fuel Cell Systems Explained, 3rd Edition John Wiley & Sons Ltd, Chichester, UK. <https://doi.org/10.1002/9781118706992>
- [2] Wang Y, Chen KS, Mishler J, Cho SC, Adroher XC (2011) A review of polymer electrolyte membrane fuel cells: Technology, applications, and needs on fundamental research. Appl. Energy 88:981–1007. <https://doi.org/10.1016/j.apenergy.2010.09.030>
- [3] Li H, Li H, Tang Y, Wang Z, Shi Z, Wu S, et al (2008) A review of water flooding issues in the proton exchange membrane fuel cell. J Power Sources 178:103–17. <https://doi.org/10.1016/j.jpowsour.2007.12.068>
- [4] Simons A, Bauer C (2011) Life cycle assessment of hydrogen production. Book Chapter, In Transition to Hydrogen—Pathways toward Clean Transportation, Wokaun A, Wilhelm E. Cambridge University Press: Cambridge, UK. <https://doi.org/10.1017/cbo9781139018036.006>
- [5] Coutanceau C, Baranton S (2016) Electrochemical conversion of alcohols for hydrogen production: a short overview. WIRE Energy and Environment, 5:388–400. <https://doi.org/10.1002/wene.193>
- [6] Selembo PA, Perez JM, Lloyd WA, Logan BE (2009) High hydrogen production from glycerol or glucose by electro-hydro genesis using microbial electrolysis cells. Int. J. Hydrogen Energy 34:5373–81. <https://doi.org/10.1016/j.ijhydene.2009.05.002>
- [7] Bambagioni V, Bevilacqua M, Bianchini C, Filippi J, Lavacchi A, Marchionni A, Vizza F, Shen PK (2010) Self-sustainable production of hydrogen, chemicals, and energy from renewable alcohols by electrocatalysis. ChemSusChem 3:851–55. <https://doi.org/10.1002/cssc.201000103>
- [8] Jiménez-Rodríguez A, Serrano A, Benjumea T, Borja R, El Kaoutit M, Feroso FG (2019) Decreasing Microbial Fuel Cell Start-Up Time Using Multi-Walled Carbon Nanotubes. Emerging Science Journal 3:109–14. <https://doi.org/10.28991/esj-2019-01174>
- [9] Santoro C, Arbizzani C, Erable B, Ieropoulos I (2017) Microbial fuel cells: From fundamentals to applications. A review. J Power Sources 356:225–44. <https://doi.org/10.1016/j.jpowsour.2017.03.109>
- [10] Parsa N, Khajouei G, Masigol M, Hasheminejad H, Moheb A (2018) Application of Electrodialysis Process for Reduction of Electrical Conductivity and COD of Water Contaminated By Composting Leachate. Civil Engineering Journal 4:1034–45. <https://doi.org/10.28991/cej-0309154>
- [11] Ali A, Ejaz N, Nasreen S, Nasir A, Qureshi LA, Al-Sakkaf BM (2019) Enhanced Degradation of Dyes present in Textile Effluent by Ultrasound-Assisted Electrochemical Reactor. Civil Engineering Journal 5:2131–42. <https://doi.org/10.28991/cej-2019-03091399>
- [12] Ellamla H, Staffell I, Bujlo P, Pollet BG, Pasupathi S (2015) Current status of fuel cell-based combined heat and power systems for the residential sector. J Power Sources 293:312–28. <https://doi.org/10.1016/j.jpowsour.2015.05.050>
- [13] Barbir F (2013) PEM Fuel Cells 2nd Edition. Academic Press Inc. Cambridge, USA. <https://doi.org/10.1016/b978-0-12-387710-9.05002-5>

- [14] Wu J, Yuan XZ, Martin JJ, Wang H, Zhang J, Shen J, Wu S, Merida W (2008) A review of PEM fuel cell durability: Degradation mechanisms and mitigation strategies. *J Power Sources* 184:104–19. <https://doi.org/10.1016/j.jpowsour.2008.06.006>
- [15] Nigmatullin RR, Martemianov S, Evdokimov YK, Denisov E, Thomas A, Adiantov N (2016) New approach for PEMFC diagnostics based on quantitative description of quasi-periodic oscillations. *Int J Hydrogen Energy* 41:12582–90. <https://doi.org/10.1016/j.ijhydene.2016.06.011>
- [16] Khazaei I, Ghazikhani M, Mohammadi M (2012) Experimental and thermodynamic investigation of a triangular channel geometry PEM fuel cell at different operating conditions. *Sci Iranica* 19:585–593. <https://doi.org/10.1016/j.scient.2011.11.039>
- [17] Martemianov S, Ilie VR, Coutanceau C (2014) Improvement of the proton exchange membrane fuel cell performances by optimization of the hot pressing process for membrane electrode assembly. *J Solid State Electrochem* 18:1261–69. <https://doi.org/10.1007/s10008-013-2273-2>
- [18] Grigoriev SA, Fedotov AA, Martemianov SA, Fateev NA (2014) Synthesis of Nanostructural Electrocatalytic Materials on Various Carbon Substrates by Ion Plasma Sputtering of Platinum Metals. *Russian J Electrochem* 50:638–646. <https://doi.org/10.1134/s1023193514070064>
- [19] Thomas A, Maranzana G, Didierjean S, Dillet J, Lottin O (2013) Measurements of electrode temperatures, heat and water fluxes in PEMFCs: conclusions about transfer mechanisms. *J Electrochem Soc* 160:F191–204. <https://doi.org/10.1149/2.006303jes>
- [20] Banerjee R, Howe D, Mejia V, Kandlikar SG (2014) Experimental validation of two-phase pressure drop multiplier as a diagnostic tool for characterizing PEM fuel cell performance. *Int J Hydrogen Energy* 39:17791–801. <https://doi.org/10.1016/j.ijhydene.2014.08.118>
- [21] Dib A, Maizia R, Martemianov S, Thomas A (2019), Statistical Short Time Analysis for Proton Exchange Membrane Fuel Cell Diagnostic-Application to Water Management. *Fuel Cells* 19:539–549. <https://doi.org/10.1002/fuce.201900060>
- [22] Astafev EA (2020) Comparison of Approaches in Electrochemical Noise Analysis Using an Air-Hydrogen Fuel Cell. *Russian J Electrochem* 56:156–162. <https://doi.org/10.1134/s1023193520020032>
- [23] Legros B, Thivel PX, Bultel Y, Nogueira RP (2011) First results on PEMFC diagnosis by electrochemical noise. *Electrochem Commun* 13:1514–16. <https://doi.org/10.1016/j.elecom.2011.10.007>
- [24] Miramontes JA, Nieves-Mendoza D, Castillo-González E, Almeraya-Calderón F (2014) Electrochemical noise analysis of nickel-based superalloys in acid solutions. *Int J Electrochem Sci* 9:523–3. <https://doi.org/10.5006/1.3294407>
- [25] Vorotyntsev MA, Martem'yanov SA, B. Grafov M (1984) Temporal correlation of current pulsations at one or several electrodes: a technique to study hydrodynamic fluctuation characteristics of a turbulent flow. *J Electroanal Chem Interfacial Electrochem* 179:1–23. [https://doi.org/10.1016/s0022-0728\(84\)80270-3](https://doi.org/10.1016/s0022-0728(84)80270-3)
- [26] Adolphe X, Danaila L, Martemianov S (2007) On the small-scale statistics of turbulent mixing in electrochemical systems. *J Electroanal Chem* 600:119–30. <https://doi.org/10.1016/j.jelechem.2006.04.023>
- [27] Martemianov S, Danaila L (2003) On the study of electrochemical turbulent noise in a stirred vessel. *Fluct Noise Letters* 3:L463–71. <https://doi.org/10.1142/s0219477503001555>
- [28] Gabrielli C, Huet F, Keddam M (1985) Characterization of electrolytic bubble evolution by spectral analysis. Application to a corroding electrode. *J Appl Electrochem* 15:503–8. <https://doi.org/10.1007/bf01059291>
- [29] Hodgson DR (1996) Application of Electrochemical Noise and In situ Microscopy to the study of Bubble evolution on chlorine evolving anodes. *Electrochim Acta* 41:605–9. [https://doi.org/10.1016/0013-4686\(95\)00347-9](https://doi.org/10.1016/0013-4686(95)00347-9)
- [30] Mansfeld F, Lee CC (1997) The Frequency Dependence of the Noise Resistance for Polymer-Coated Metals. *J Electrochem Soc* 144:2068–71. <https://doi.org/10.1149/1.1837743>

- [31] Bertocci U, Frydman J, Gabrielli C, Huet F, Keddam M (1998) Analysis of Electrochemical Noise by Power Spectral Density Applied to Corrosion Studies Maximum Entropy Method or Fast Fourier Transform. *J Electrochem Soc* 145:2780–86. <https://doi.org/10.1149/1.1838714>
- [32] Gabrielli C, Keddam M (1992) Review of applications of impedance and noise analysis to uniform and localized corrosion. *Corrosion* 48:794–811. <https://doi.org/10.5006/1.3315878>
- [33] Gabrielli C, Huet F, Keddam M (1986) Investigation of electrochemical processes by an electrochemical noise analysis. Theoretical and experimental aspects in potentiostatic regime. *Electrochim Acta* 31:1025–39. [https://doi.org/10.1016/0013-4686\(86\)80018-4](https://doi.org/10.1016/0013-4686(86)80018-4)
- [34] Denisov ES, Evdokimov YK, Martemianov S, Thomas A, Adiutantov N (2016) Electrochemical noise as a diagnostic tool for PEMFC. *Fuel Cells* 17:225–37. <https://doi.org/10.1002/fuce.201600077>
- [35] Astafev EA, Ukshe AE, Gerasimova EV, Dobrovolsky YA, Manzhos RA (2018) Electrochemical noise of a hydrogen-air polymer electrolyte fuel cell operating at different loads. *J Solid State Electrochem* 22:1839–1849. <https://doi.org/10.1007/s10008-018-3892-4>
- [36] Huet F, Nogueira RP, Lailler P, Torcheux L (2006) Investigation of the high-frequency resistance of a lead-acid battery. *J Power Sources* 158:1012–18. <https://doi.org/10.1016/j.jpowsour.2005.11.026>
- [37] Martemianov S, Adiutantov N, Evdokimov YK, Madier L, Maillard F, Thomas A (2015) New methodology of electrochemical noise analysis and applications for commercial Li-ion batteries. *J Solid State Electrochem* 19:2803–10. <https://doi.org/10.1007/s10008-015-2855-2>
- [38] Astafev EA (2020) The measurement of electrochemical noise of a Li-ion battery during charge-discharge cycling. *Measurement* 154:107492. <https://doi.org/10.1016/j.measurement.2020.107492>
- [39] Greisiger H, Schauer T (2000) On the interpretation of the electrochemical noise data for coatings. *Prog Org Coat* 39:31–6. [https://doi.org/10.1016/s0300-9440\(00\)00096-5](https://doi.org/10.1016/s0300-9440(00)00096-5)
- [40] Xiao H, Mansfeld F (1994) Evaluation of coating degradation with electrochemical impedance spectroscopy and electrochemical noise analysis. *J Electrochem Soc* 141:2332–7. <https://doi.org/10.1149/1.2055121>
- [41] Bahrami MJ, Shahidi M, Hosseini SMA (2014) Comparison of electrochemical current noise signals arising from symmetrical and asymmetrical electrodes made of Al alloys at different pH values using statistical and wavelet analysis. Part I: Neutral and acidic solutions. *Electrochim Acta* 148:127–44. <https://doi.org/10.1016/j.electacta.2014.10.031>
- [42] Aballe A, Bethencourt M, Botana FJ, Marcos M (1999) Using wavelets transform in the analysis of electrochemical noise data. *Electrochim Acta* 44:4805–16. [https://doi.org/10.1016/s0013-4686\(99\)00222-4](https://doi.org/10.1016/s0013-4686(99)00222-4)
- [43] Lentka L, Smulko J (2019) Methods of trend removal in electrochemical noise data – Overview *Measurement*. 131:569–581. <https://doi.org/10.1016/j.measurement.2018.08.023>
- [44] Grafov BM, Dobrovolskij YA, Kluev AL, Ukshe AE, Davydov AD, Astaf'ev EA (2017) Median Chebyshev spectroscopy of electrochemical noise. *J Solid State Electrochem* 21:915–918. <https://doi.org/10.1007/s10008-016-3395-0>
- [45] Martemyanov SA, Petrovskiy NV, Grafov BM (1991) Turbulent pulsations of the microelectrode limiting diffusion current. *J Applied Electrochemistry* 21:1099–102. <https://doi.org/10.1007/bf01041455>
- [46] Martemianov S (2017) Statistical Theory of Turbulent Mass Transfer in Electrochemical Systems. *Russian J Electrochem* 53:1076–1086. <https://doi.org/10.1134/s1023193517100081>
- [47] Kay SM, Marple SL (1981) Spectrum analysis—A modern perspective. *Proceedings of the IEEE* 68(11). [doi: 10.1109/PROC.1981.12184](https://doi.org/10.1109/PROC.1981.12184)
- [48] Maizia R., Dib A., Thomas A., Martemianov S. (2017) Proton exchange membrane fuel cell diagnosis by spectral characterization of the electrochemical noise. *Journal of Power Sources* 342: 553-561. <https://doi.org/10.1016/j.jpowsour.2016.12.053>

List of Symbols

EN - electrochemical noise
ENA - electrochemical noise analysis
PEMFC - Proton Exchange Membrane Fuel Cell
MEA - Membrane Electrode Assembly
PSD - Power Spectral Density

Sub/superscripts

1	Zone 1 of the campaign measurements
2	Zone 2 of the campaign measurements
2,1	Part 1 of zone 2 of the campaign measurements
2,2	Part 2 of zone 2 of the campaign measurements
2,3	Part 3 of zone 2 of the campaign measurements
85	Current of 85A

Parameters and Variables

α	power factor of fractional noise (PSD linear slope in logarithmic coordinates)
f	Frequency / Hz
T	Time / sec or hour