

## **Electrochemical pressure impedance spectroscopy for investigation of mass transfer in polymer electrolyte membrane fuel cells**

A.V. Shirsath<sup>1</sup>, S. Raël<sup>1</sup>, C. Bonnet<sup>1</sup>, L. Schiffer<sup>2</sup>, W. Bessler<sup>2</sup>, F. Lapicque<sup>1, \*</sup>

<sup>1</sup> Reactions and Chemical Engineering Laboratory, CNRS-University of Lorraine, 1 rue Grandville, 54000 Nancy, France

<sup>2</sup> Institute of Energy Systems Technology (INES), Offenburg University of Applied Sciences, Badstrasse 24, 77652 Offenburg, Germany

### **Abstract:**

Mass transfer phenomena in membrane fuel cells are complex and diversified, because of the presence of complex transport pathways including porous media of very different pore sizes, and possible formation of liquid water. Electrochemical impedance spectroscopy, although allowing valuable information on ohmic, charge and mass transfer phenomena, may nevertheless appear insufficient below 1 Hz. Use of another variable i.e. back pressure as excitation variable for electrochemical pressure impedance spectroscopy is shown here a promising tool for investigations and diagnosis of fuel cells.

**Keywords:** Impedance spectroscopy; Pressure oscillations; Fuel cells; Mass transfer phenomena; Liquid water.

(\*) Correspondence: Dr. François Lapicque

[francois.lapicque@univ-lorraine.fr](mailto:francois.lapicque@univ-lorraine.fr)

## **Introduction to transfer phenomena investigations in fuel cells**

Polymer electrolyte membrane fuel cells (PEMFC) in addition to being an attractive system for energy conversion, represent a huge research area for electrochemists and engineers, combining electrode mechanisms and kinetics to transport or transfer phenomena in the various porous media and flow channels of the cell. Progress in the understanding of the physical phenomena involved, actually allowed progressive, however huge improvement in fuel cell performance and efficiency. The porous materials in PEMFCs comprise the catalyst layer formed by a nanostructured carbon material supporting the catalyst clusters, and the gas diffusion layer in contact to the bipolar plates, which allow gas distribution in the fuel cell. In most current technologies, gas diffusion layers are carbon-based and consist of a macroporous substrate with 10-30  $\mu\text{m}$  pores with a microporous layer directly in contact with the catalyst layer.

Modelling of the fuel cell core was initiated in the 1980s through the description of porous electrodes, where the catalyst is in the form of a thin film on the surface of the pores, or as agglomerates in a parallel-piped porous structure [1, 2]. Numerous works published since then could refine the pioneering approaches for more accurate representation of the catalyst layer [3-5], before more complete theoretical works could integrate physical phenomena occurring in the non-reactive gas diffusion layer.

## **Electrochemical impedance spectroscopy (EIS) for mass transfer phenomena in PEMFC**

EIS featuring the ratio of complex voltage over current fluctuations over a large range of frequencies can show the occurrence of ohmic phenomena for frequency on the order of 1 kHz, charge transfer at lower frequencies, then mass transfer phenomena for frequencies at the Hz level or below. As for other electrochemical systems, EIS spectra of fuel cells in the Nyquist plot often consist of two main loops – with possible overlapping -, the first one in the high frequency range expressing finite charge transfer rates while the second one is usually believed to be related to control by mass transfer phenomena [4], [6-9]. The most simple model for mass transfer derives from Fick's second law, whose complex impedance solution involves a resistance, the value of which expressing the significance of mass transfer control, and a time constant indicating on the frequency range for this loop. This time constant, which is given as the ratio of the square of a characteristic length and the effective diffusivity of the electrochemical species, indicates on the frequency range of the mass transfer phenomenon.

The above ideal description of Nyquist EIS spectra does not hold in all cases, because of the occurrence of more complex processes as discussed here.

Mass transfer processes in fuel cells cover various physicochemical phenomena in the different cell components, involving gaseous reactants or the water produced, as exemplified below.

- In the catalyst layer, in addition to the refined modelling approaches of the catalyst layer, one can mention use of EIS for evaluation of improved catalyst layer deposition [10], or fundamental investigations on the importance of the nature of the pore filling liquid [11] or the specific roles of catalyst clusters and carbon support [12]. Moreover, in addition to its transport in the catalyst layer pores, the reacting gas dissolves in the thin ionomeric layer attached to the catalyst cluster for possible charge transfer, accompanied by  $H^+$  transfer: the set of process is often viewed by EIS as an overall single phenomenon, with signature in the high-frequency loop. The lumped nature of the charge and mass transfer in the catalyst layer often results in a single loop in the Nyquist plot, making its interpretation uneasy or little accurate. Aside mass transport, adsorption of intermediate species such as hydrogen peroxide or platinum oxides on the electrode surface [9, 13], is known to result in an inductive small loop below 1Hz
- Whereas gas transport in the channels of the distribution (bipolar plates) is often a fast process, it is often believed to be rate-controlling in the gas diffusion layer structure. Linked to the gas permeability and the pore size, gas transport rates in the MPL – often reported as helping in the water management in the cell [14-16] are to differ strongly from those in the macroporous substrate. Modeling the overall transfer rates for a microporous layer-coated substrate by a single time constant approach can reveal as inefficient, because of very different pore size distributions and permeability exhibited by the two layers [17].
- Whereas drying conditions have to be avoided, presence of liquid water (flooding) can be problematic as hindering gas transport, and even hazardous for fuel cell operation and durability. EIS has been proven an efficient diagnosis for occurrence of both undesired situations. In essence, drying is observed by increased impedance in the whole frequency range, whereas only the low frequency loop in the Nyquist plot is enlarged by occurrence of flooding [18-20]. Besides, liquid flow in the cell is per se discontinuous, as slug flow in the channels and being an “eruptive” transport in the carbon layers [21, 22]. Because of the little deterministic nature of liquid transport, Roy and Orazem [23] developed a stochastic approach in EIS, flooding being revealed by far larger EIS data scattering at a fixed frequency.

EIS is usually not conducted alone to characterise the operation or the state of health of fuel cells: other electrochemical techniques e.g. voltage measurement at fixed current density (cd), cyclic or sweep voltammetry are routinely employed in complement to EIS, as well as –more recently - estimation of the limiting cd [10, 24]. Mechanical, analytical, spectroscopic and microscopic techniques can help in establishing reliable diagnosis on a fuel cell [25, 26]. In particular, the significant issue of liquid water in the cell structure can benefit from spectroscopic techniques e.g. NMR [27], neutron imaging and synchrotron X-ray. Synchrotron X-ray can provide local saturation in liquid water with image resolution below 10  $\mu\text{m}$  in gas diffusion layer and electrode structures [20], [28-30], in particular revealing far higher saturations over the ribs than over the channel [31].

EIS although powerful may appear insufficient to explore mass transfer phenomena because of the often limited information drawn from spectra in the low frequency domain. Besides, in some cases, an inductive loop below a few Hz often corresponds to adsorption processes, which can interfere with the signature of mass transfer phenomena.

Impedance spectroscopy in electrochemistry is not restricted to correlation of current and potential: other physical variables have successfully used such as pulsation of velocity in electrohydrodynamic impedance [32], or the sine weight fluctuations monitored by a quartz balance upon potential modulation [33]. Moreover, it has recently been suggested to extend dynamic diagnostics in cells with gaseous reactants or products to the pressure at the cell outlet. This led to the concept of electrochemical pressure impedance (or pressure-induced electrochemical) spectroscopy (EPIS) introduced by Hartmann et al. [34]. Development of this promising technique for investigations of low frequency phenomena occurring in a fuel cell is introduced below.

### **Pressure-induced impedance spectroscopy for fuel cell behaviour in the low frequency range**

Gas pressure is known to be an asset to performance of fuel cells: increase in the pressure has a positive effect on the zero-current cell voltage, exchange current density and mass transfer rates [35, 36]. The dynamics relationship between pressure and the cell voltage was shown in [37, 38] for the case of sodium-air batteries, with various impedances defined between two variables amongst voltage, current and pressure, the third one being kept constant. The potential of EPIS was soon confirmed by simulation [38], before EPIS – here defined as the ratio of

voltage fluctuations over back pressure oscillations,  $Z_{V/p}$  - was successfully performed on a fuel cell using a loudspeaker to generate pressure oscillations below 100 Hz [39], although the experimental spectra were presumably subject to considerable noise.

### EPIS: the techniques used

Because of the above limitations of EIS for frequencies below 1 Hz for distinct analysis of mass transfer phenomena, EPIS has been investigated through experiments and simulations in view to evaluating its potential as accurate diagnosis tool with distinct analysis of rate-controlling mass transfer processes below 1 Hz.

Experimental EPIS spectra were recorded in a 100 cm<sup>2</sup> single FC (UBzM) installed in a fully equipped test bench, for operation at controlled back pressure, with sustained fluctuations of the cathode outlet and at constant current [40]. Air was humidified at various levels in thermostated double-walled vessel. Stoichiometry factors for H<sub>2</sub> and air O<sub>2</sub> at 1.2 and 2.5 respectively, and the cell was operated at 55°C with a steady pressure at 1.15 bar. The whole system was controlled a D-space card with Matlab-Simulink environment. Fluctuating response of the potential was recorded. Back pressure amplitude was carefully selected depending on the frequency in the range 1 mHz – 1 Hz to allow linear behaviour of the system through low distorted voltage signal, and appreciable voltage amplitude [40]. In complement, an EPIS model based on the in-house code DENIS [38, 41] with a (1D+1D) model has been developed, with Navier-Stokes equation for gas transport in the channels and diffusion-convection equation in the gas diffusion layers [41, 42]. The electrode is considered as flat at the membrane interface, and water transport in the membrane covers electroosmotic drag and back-diffusion.

### Preliminary results and conclusions

Comparison of EIS and EPIS is shown on an example in Figure 1 in both Bode and Nyquist plot. The modulus of  $Z_{V/p}$  exhibits a sigmoidal variation with the frequency, being at a fraction of  $\mu\text{V}/\text{Pa}$  at a few mHz and attaining 5  $\mu\text{V}/\text{Pa}$  at 1 Hz. In agreement with data in [37], the phase shift angle decreased regularly from nearly 0° at 1 mHz to approx. 190° at a Hz. On the contrary, corresponding EIS spectra  $Z_{V/I}$  exhibit conventional profiles (Fig. 1c and d), in particular showing very little changes below 1Hz.

Water management investigations in the test bench showed that for low air humidification (RH=20%), no liquid water is formed in the cell, whereas for fully hydrated air, the production rate of liquid formed is nearly proportional to the cd. At low cd, EPIS modulus increases with the excitation frequency, with little effect of the hydration level (Fig. 2a). On the contrary, at

high cd ( $1 \text{ A/cm}^2$ ), the presence of liquid water is visible in EPIS spectra below 50 mHz, whereas the impedance is far less affected by the relative humidity for higher frequencies (Fig. 2b). In all cases, the phase shift angle followed similar variations in all hydration and cd conditions.

The pressure dynamics within the cell can be influenced by other system components. We have therefore investigated the dynamic ratio of fuel cell inlet over fuel cell outlet pressure,  $Z_{p(\text{in})/p(\text{out})}$ . In the model we have included a 0-D humidifier upstream of the cell. Boundary conditions were constant mass flow into the humidifier and oscillating back pressure at fuel cell outlet. Figure 3 shows a comparison of experimental and simulated  $Z_{p/p}$  spectra. The data show a drop in modulus at around 0.1 Hz, associated with a drop in phase angle from  $0^\circ$  to  $-90^\circ$ . By varying the humidifier volume in the model, we could show that this response is dominated by the humidifier. We conclude that the pressure response of balance-of-plant components need to be included into the EPIS interpretation.

These preliminary data show the potential of EPIS for transport/transfer investigation in fuel cells in the low frequency domain, which can be a complementary technique with a technology based on simple mechanical devices (loudspeakers or pressure valves), far cheaper than spectroscopic equipments.

## Acknowledgments

The work was partially funded by the German Research Federation (DFG) (no. 391377080) and French National Research Agency in the frame of Epistel project (ANR-2017)

Figure 1. Comparison of EPIS measurements at  $0.4 \text{ A/cm}^2$ , air humidified at 55%;  $T(\text{fuel cell}) = 55^\circ\text{C}$ ; (a) Bode plot (b) Nyquist plot, with EIS measurements (c) Bode plot (d) Nyquist plot. The solid lines in Nyquist plots b) and d) are only for illustrative purpose, not related to modelling

Figure 2. Modulus of the voltage-over-pressure impedance at two cd levels, depending on the relative humidity (RH) of the air injected; (a), top,  $0.2 \text{ A/cm}^2$ ; (b), bottom  $1 \text{ A/cm}^2$

Figure 3. Comparison of experimental and simulated dynamic pressure response  $Z_{p(\text{in})/p(\text{out})}$  of the fuel cell test bench including the humidifier. Values for the gas phase volume are given in liter in the figure.

## Literature cited

- [1] M. Watanabe, M. Takao, Y. Namekawa, Controlled micropore distribution of porous gas-diffusion electrodes for a molten carbonate fuel cell by a slurry sintering method, *Denki Kagaku*, 57(6) (1989) 586-590
- [2] T.E. Springer, I.D. Raistrick, Electrical impedance of a pore-wall for the flooded-agglomerate model of porous gas-diffusion electrodes, *J. Electrochem. Soc.* 136 (1989) 1594
- [3] T.E. Springer, M.S. Wilson, S. Gottesfeld, Modeling and experimental diagnostics in polymer electrolyte fuel cells, *J. Electrochem. Soc.* 140 (1993) 3513-3526.
- [4] (\*) T.E. Springer, T.A. Zawodzinski, Characterization of polymer electrolyte fuel cells using AC impedance spectroscopy, *J. Electrochem. Soc.* 143 (1996) 587-589. *One of the first extensive experimental investigations of the various phenomena in fuel cells by impedance spectroscopy, from conductivity in the membrane to estimation of the effective tortuous path length to gas diffusion in the carbon layers.*
- [5] Y. Bultel, P. Ozil, R. Durand, Modified thin film and agglomerate models for active layers of P.E. fuel cells, *Electrochem. Acta* 43 (9) (1998) 1077-1087.
- [6] C.J. Brug, A.L.G. van den Eeden, M. Sluyters Rehbach, J.H. Sluyters, The analysis of electrode impedances complicated by the presence of a constant phase element, *J. Electroanal. Chem.* 176 (1984) 275-295.
- [7] (\*) P. Agarwal, M.E. Orazem, I.H. Garcia-Rubio, Critical issues associated with interpretation of impedance spectra, *J. Electroanal. Chem.* 378 1-2 (1994) 51-62. *The critical paper on interpretation of EIS spectra, demonstrated the non-uniqueness of impedance models. Additional experiments under modified operating conditions or with other techniques, together with thorough statistical treatment of the data, can enhance the accuracy and the significance of the model.*
- [8] E. Barsoukov and J.R. Macdonald Eds, *Impedance spectroscopy: theory, experiments and applications*, New Jersey, J. Wiley & Sons (2005).
- [9] M.E. Orazem and B. Tribollet, *Electrochemical impedance spectroscopy*, 2<sup>nd</sup> Edition, New Jersey, J. Wiley & Sons (2017).
- [10] J. J. Conde, M.A. Folgado, P. Ferreira-Aparicio, A.M. Chaparro, A. Chowdhury, A. Kusoglu, D. Cullen, A.Z. Weber, Mass-transport properties of electrosprayed Pt/C catalysts layers for polymer-electrolyte fuel cells, *J. Power Sources* 427 (2019) 250-259.
- [11] M.B. Ji, Z.D. Wei, S.G. Chen, M.R. Xia, Q. Zhang, X.Q. Qi, X.H. Hu, W. Ding, L. Li, Electrochemical impedance spectroscopy evidence of dimethyl-silicon-oil enhancing O<sub>2</sub> transport in a porous electrode, *Electrochim. Acta* 56 (2011) 4797-4802.
- [12] Q. Meyer, Y. Zeng, C. Zhao, Electrochemical impedance spectroscopy of catalyst and carbon degradations in proton exchange membrane fuel cells, *J. Power Sources* 437 (2019) 226922.

- [13] S.K. Roy, H. Hagelin-Weaver, M.E. Orazem, Application of complementary analytical tools to support interpretation of polymer electrolyte membrane fuel cell impedance data, *J. Power Sources*, 196 (2011) 3736-3742.
- [14] A. El-Kharouf, B.G. Pollet, Gas diffusion media and their degradation, in *Polymer electrolyte fuel cell degradation*, Eds. M.M. Mench, E.C. Kumber and T.N. Verziroglu, Academic Press, New-York (2012) 215-247.
- [15] E. Nishiyama, T. Murahashi, Water transport characteristics in the gas diffusion media of proton exchange membrane fuel cell – Role of the microporous layer, *J. Power Sources* 196 (2011) 1847-1854.
- [16] F. Lapique, M. Belhadj, C. Bonnet, Y. Thomas, J. Pauchet, A critical review on gas diffusion micro-and macroporous layer degradations for improved membrane fuel cell durability, *J. Power Sources* 136 (2016) 40-53.
- [17] D. Malevich, E. Halliop, B.E. Peppley, J.G. Pharoah, K. Karan, Investigation of charge-transfer and mass-transport resistances in PEMFCs with microporous layer using electrochemical impedance spectroscopy, *J. Electrochem. Soc.* 156 (2009) B216-B222.
- [18] W. Merida, D.A. Harrington, J-M. Le Canut, G.McLean, Characterisation of proton exchange membrane fuel cell (PEMFC) failures via electrochemical impedance spectroscopy, *J. Power Sources* 161 (2006) 266-274.
- [19] N. Fouquet, C. Doulet, C. Nouillant, G. Dauphin-Tanguy, B. Ould-Bouamama, Model based PEM fuel cell state-of-health monitoring via ac impedance measurements, *J. Power Sources*, 159 (2006) 905-913.
- [20] P. Antonacci, S. Chevalier, J. Lee, R. Yip, N. Ge, A. Bazylak, Feasibility in combining electrochemical impedance spectroscopy and synchrotron X-ray radiography for determining the influence of liquid water on polymer electrolyte membrane fuel cell performance, *Int. J. Hydrogen Energ.* 40 (2015) 16494-16502.
- [21] T.H. Haines, Water transport across biological membranes, *FEBS Lett.* 346 (1994) 115-122.
- [22] I. Manke, C. Hartnig, M. Grünerbel, W. Lehnert, N. Kardjilov, A. Haibel, A. Hilger, J. Banhart, H. Riesermeier, Investigation of water evolution and transport in fuel cells with high resolution synchrotron R-Ray radiography, *Appl. Phys. Lett.* 90 (2007) 174015.
- [23] S.K. Roy and M.E. Orazem, Analysis of flooding as a stochastic process in polymer electrolyte membrane (PEM) fuel cells by impedance techniques, *J. Power Sources*, 184 (2008) 212-219.
- [24] A. Chowdhury, C.J. Radke, A.Z. Weber, Transport resistances in fuel-cells catalyst layers, *Polymer electrolyte fuel cells 17 (PEFC 17) Book Series; ECS Transactions*, 80 (8) (2017) 321-333.
- [25] I.A. Schneider, H. Kuhn, A. Wokaun, G.G. Scherer, Fast locally resolved electrochemical impedance spectroscopy in polymer electrolyte fuel cells, *J. Electrochem. Soc.* 152, 10 (2005) A2092-2103.
- [26] S. Rozeai Niya, M. Hoorfar, Study of proton exchange membrane fuel cells using electrochemical impedance spectroscopy technique – A review, *J. Power Sources*, 240 (2013) 281-293.



- [27] X. Yuan, H. Wang, J.C. Sun, J. Zhang, A.C. Impedance technique in PEM fuel cell diagnosis- A review, *Int. J. Hydrogen Energ.* 32 (2007) 4365-4380
- [28] J. Cho, J. Park, H. Oh, K. Min, E. Lee J-Y. Jyoung, Analysis of the transient response and durability characteristics of a proton exchange membrane fuel cell with different micro-porous layer penetration thicknesses, *Appl. Energy* 111 (2013) 300-309.
- [29] S. Chevalier, J. Lee, R. Yip, P. Antinacci, Y. Tabuchi, T. Kotaka, A. Bazylak, In-operando measurements of liquid water saturation distributions and effective diffusivities of polymer electrolyte membrane fuel cell gas diffusion layers, *Electrochim. Acta* 210 (2016) 792-803.
- [30] H. Liu, M.G. Georges, N. Ge, D. Muirhead, P. Shreshtha, J. Lee, R. Banerjee, R. Zeis, M. Messerschmidt, M. Scholta, Microporous Layer Degradation in Polymer Electrolyte Membrane Fuel Cells, *J. Electrochem. Soc.* 165(6) (2018) F3271-F3280
- [31] D. Ge, P. Shrestha, M. Balakrishnan, D. Ouelette, A.K.C. Wong, H. Liu, C.H. Lee, J.K. Lee, A. Bazylak, Resolving the gas diffusion layer substrate land and channel region contribution to the oxygen transport resistance of a partially-saturated substrate, *Electrochim. Acta*, 328 (2019) 135001.
- [32] C. Deslouis, O. Gil, B. Tribollet, G. Vlachos, B. Robertson, Oxygen as a tracer for measurements of steady and turbulent flows, *J. Appl. Electrochem.* 22 (1992) 835-842.
- [33] S. Bourkane, C. Gabrielli, M. Keddam, Investigation of gold oxidation in a sulphuric medium: electro-gravimetric transfer function technique, *Electrochim. Acta* 38, 14 (1993) 1827-1835.
- [34] (\*) P. Hartmann, D. Gröbl, H. Sommer, J. Janek; WG. Bessler, P. Adelhelm, Pressure dynamics in metal-oxygen (metal-air) batteries: a case study on sodium superoxide cells, *J. Phys. Chem. C*, 118, 3 (2014) 1461-1471. *This pioneering paper deals with measuring the pressure dynamics in the gas reservoir of a sodium-air battery: analysis of cyclic voltammetric experiments in a broad scanning rate range allowed electrochemical pressure impedance spectroscopy to be introduced.*
- [35] T. Reshchenko, A. Kulikovski, PEM Fuel cell characterization by means of the physical model for impedance spectra, *J. Electrochem. Soc.* 162(7) (2015) F627-F633.
- [36] J. Zhang, C. Song, J. Zhang, R. Baker, L. Zhang, Understanding the effects of back-pressure on PEM fuel cells reactions and performances, *J. Electroanal. Chem.* 68 (2013) 130-136.
- [37] A.M. Niroumand, W. Merida, M. Eikerling, M. Saif, Pressure-voltage oscillations as a diagnostic tool for PEFC cathodes, *Electrochem. Comm.* 75 (2017) 60-63.
- [38] (\*) D. Gröbl, J. Janek, W.G. Bessler, Electrochemical pressure impedance spectroscopy (EPIS) as diagnostic method for electrochemical cells with gaseous reactants: a model based analysis, *J. Electrochem. Soc.* 163(5) (2016) A599-A610. *Considering various electrochemical cells with gaseous reactants or products, the authors established the various impedance combinations with the cell pressure, though a model-based study of electrochemical pressure impedance spectroscopy featuring the dynamics of electrical and non-electric variables.*

- [39] E. Engebretsen, T.J. Mason, P.R. Shearing, G. hinds, D.J.L. Brett, Electrochemical pressure impedance spectroscopy applied to the study of ^polymer electrolyte fuel cells, *Electrochem. Comm.* 75 2017) 60-63.
- [40] A. Shirsath, S. Raël, C. Bonnet, F. Lapique, Pressure-induced electrochemical spectroscopy in polymer electrolyte fuel cells: role of back pressure in the analysis of mass transport phenomena, in preparation.
- [41] W. Bessler, S. Gewies, M. Vogler, A new framework for physically based modeling of solid oxide fuel cells, *Electrochim. Acta*, 53(4) (2007) 1782-1800.
- [42] L. Schiffer, D. Grübl, W. Bessler, Model-based analysis of electrochemical pressure impedance spectroscopy (EPIS) for PEM Fuel Cells. In: H.A. Gasteiger und A. Bandarenka (Eds): EFCF 2019. Proceedings of the European Fuel Cell Forum: low-temperature fuel cells, electrolysers, Luzern (2019).