Journal of Power Sources 326 (2016) 112–119

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Review article

Inductive phenomena at low frequencies in impedance spectra of proton exchange membrane fuel cells – A review

Ivan Pivac, Frano Barbir*

Faculty of Electrical Engineering, Mechanical Engineering and Naval Architecture, University of Split, 21000 Split, Croatia

HIGHLIGHTS

- Different causes of inductive phenomena in fuel cells are reviewed and discussed.
- Side reactions with intermediate species and/or water transport most likely causes.
- New equivalent circuits with physical meaning of each element are needed.

ARTICLE INFO

Article history:
Received 26 April 2016
Accepted 28 June 2016

Keywords:
Electrochemical impedance spectroscopy
Inductive phenomena
Inductive loop
Side reactions
Water transport

ABSTRACT

The results of electrochemical impedance spectroscopy of proton exchange membrane (PEM) fuel cells may exhibit inductive phenomena at low frequencies. The occurrence of inductive features at high frequencies is explained by the cables and wires of the test system. However, explanation of inductive loop at low frequencies requires a more detailed study. This review paper discusses several possible causes of such inductive behavior in PEM fuel cells, such as side reactions with intermediate species, carbon monoxide poisoning, and water transport, also as their equivalent circuit representations. It may be concluded that interpretation of impedance spectra at low frequencies is still ambiguous, and that better equivalent circuit models are needed with clearly defined physical meaning of each of the circuit elements.

1. Introduction

Electrochemical impedance spectroscopy (EIS) is a well-known method for modeling and diagnosis of proton exchange membrane fuel cells (PEMFCs), which enables *in situ* identification and quantification of physical phenomena that influence fuel cell performance [1–6]. The general approach is to stimulate the object under observation with a known alternating current or voltage signal and consequently measure the response of the system. By analyzing the impedance, which is opposition to the flow of alternating current, over a range of frequencies, it is possible to untangle simultaneous processes happening at different rates.

One of the first literature reviews conducted in the field of EIS investigations on PEMFCs is the work published by Gomadam and Weidner [7] in 2005. They have placed emphasis on the papers that analyze and model the impedance response of the cathode and anode half-cells based on a continuum-mechanics approach (involves mathematical descriptions of physical and electrochemical phenomena derived from conservation equations using first principles), while the papers based on an equivalent-circuits approach (involves network of different electrical analogues, whose values are obtained by fitting procedures to experimental data) were outlined and briefly discussed with the relative advantages and disadvantages of the two approaches. Another review paper, and one of the most comprehensive reviews in this field, is the work published by Yuan et al. [8] in 2007. They discussed various measurement and feeding modes in EIS on PEMFCs, as well as interpretation, and EIS applications in optimization and contamination effects. Recent review paper, published by Rezaei Niya and Hoorfar [9] in 2013, thoroughly reviews the recent efforts published in this field, as well as aspects like Kramer-Kronig relations, and process and measurement models, which were not covered in Ref. [8]. The paper also highlighted the novel studies performed and ideas developed based on the EIS method, the recent EIS applications, and finally discussed common uncertainties and possible errors in the interpretation of the EIS measurements. However, in the

* Corresponding author.
E-mail addresses: ipivac@fesb.hr (I. Pivac), fbarbir@fesb.hr (F. Barbir).

http://dx.doi.org/10.1016/j.jpowsour.2016.06.119
0378-7753/

present paper, the studies conducted on fuel cells, mainly PEMFCs, using EIS to investigate inductive phenomena at low frequencies in impedance spectra are reviewed.

The results of electrochemical impedance spectroscopy of PEM fuel cells may exhibit inductive phenomena at low frequencies (as shown in Fig. 1) as an additional loop crossing on the positive side of the Im(Z) axis. The occurrence of inductive features at high frequencies is explained by the cables and wires of the system, which are not an integral part of the fuel cell. However, explanation of inductive phenomena at low frequencies requires a more detailed study. It is frequently observed in the literature that the slope of the polarization curve does not match the low-frequency intercept (at ca. 0.1–1 Hz) of EIS experiments [10]. The remaining inconsistency is explained by a low-frequency inductive loop, the beginning of which can be observed in EIS experiments extended below 0.1 Hz. In Fig. 1 the low frequency resistance is marked as total resistance, but it is the DC point that corresponds to the slope of the polarization curve at the current density at which the EIS was taken. However, the DC point is virtually impossible to record due to the equipment limitations. The last measurable point in Fig. 1 was taken at 10 mHz.

Roy and Orazem [11] showed that once steady-state operation was achieved, the low-frequency inductive loops in the impedance response could be associated with some unspecified physical processes (not with non-stationary phenomena) occurring within the fuel cell. In the literature, most of works containing EIS investigations [12–24] did not show any low frequency inductive loop in impedance measurements, and only a handful of studies show inductive points or an inductive loop as an interesting research object. The low frequency ranges of the Nyquist plot are affected by higher capacitances in the equivalent circuit models, which are equivalent to larger time constants, and hence slower reactions. Since the most important and controlling reactions of the fuel cell are the slowest reactions, the measured impedances in low frequencies are the most important part of the plot and provide useful information although its uncertainty is higher due to longer measuring time [9]. Although the measurements in the low frequencies are in a way that the system is changing gradually during acquisition, the frequency range cannot be restricted to higher levels and the experimental setup needs to be modified in a way that the low frequencies can be captured in quasi-stable conditions [9]. Also, the inductive loop must be accounted for to obtain consistent parameters when fitting a model to experimental impedance measurements and steady-state results, especially in the case of kinetic inductive loops [25].

Several explanations of the occurrence of these inductive phenomena have been proposed so far. In general, the origin of the low-

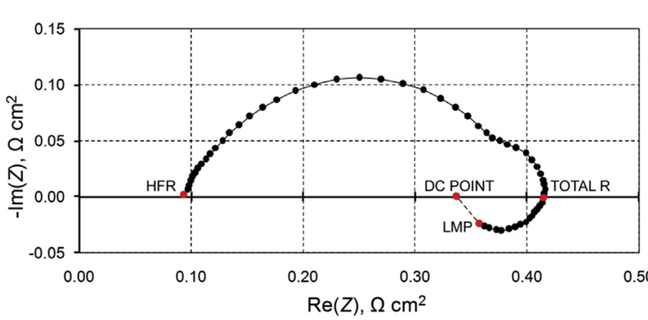

Fig. 1. Typical Nyquist plot of the measured impedance data of a H_2/Air PEM fuel cell (50 cm^2, 65 °C, 0.5 bar(g), 15 A, H_2/Air stoichiometry 2/4, 100% RH) with red-marked intercept points: high-frequency resistance (HFR), Total R, DC point, and the last measured point (LMP). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

frequency inductive loops have been considered as a characteristic of systems containing consecutive heterogeneous side reactions with several potential-dependent adsorbed intermediate reaction species [10,25–30], which can degrade fuel cell components such as membranes and electrodes. Thereby, they are reducing the lifetime, one of the crucial issues in the commercialization of fuel cell, also as the contaminating influence of carbon monoxide poisoning on platinum at constant load [31,32]. This pseudo–inductive behavior increases with time and could be coupled to a surface relaxation process at the anode due to competitive oxidation of hydrogen and carbon monoxide. However, the anode and cathode gases were mainly used rated ultrapure, so the influence of carbon monoxide could be excluded from the most investigations. On the other hand, some recent studies connect the low–frequency inductive loop to water transport characteristics in the membrane [33–39]. Several investigations were conducted on PEM fuel cell stacks [40–44] with an experimental evidence of the inductive loops, some additional modeling studies, but referencing on the previous occurrence explanations of the phenomena. Additionally, some other inductive loop investigations on direct methanol fuel cells (DMFCs) [45–48] and phosphoric acid fuel cells (PAFCs) [49] are also reviewed to give the other view on this inductive phenomenon, which is present in other similar technologies.

Consequently, current models for impedance response are limited, and only a few can lead to specific features such as the low-frequency inductive loops. Physical meaning of their elements are often incomplete, ambiguous or insufficiently validated with quantitative comparisons between the models and the corresponding experimental results. This increases the likelihood that the physical meaning of certain element is assigned to the wrong process due to a missing element in a model. Also, in many cases the same elements are completely differently interpreted. Therefore, for better understanding of inductive phenomena at low frequencies in impedance spectra of PEM fuel cells, a more thorough and comprehensive analysis is required.

2. Different causes of inductive phenomena

2.1. *Side reactions with intermediate species*

One of the first appearances of the inductive loop at low frequencies in Nyquist diagrams of PEM fuel cells was noticed in the EIS investigation by Antoine et al. [26]. They related the specific low frequency inductive behavior of the cathode impedance to the second relaxation of the adsorbed intermediate species in the oxygen reduction reaction (ORR) mechanism. This inductive loop is specific to the presence of (at least) two electrochemical steps in the ORR mechanism, and is only slightly modified by the diffusion effect. After a fast chemical O_2-adsorption step considered at equilibrium and involving a very low partial coverage, there is the first electrochemical step that corresponds to protonation of the O_2 molecule, which is the rate determining step (RDS), where the main adsorbed oxygenated intermediate species are probably O_{ads}, OH_{ads} and O_2H_{ads}. When the overpotential value increases, the inductive loop becomes proportionally more pronounced and corresponds to kinetics, adsorbed oxygenated intermediate species relaxation and diffusion. Modeling was performed by the flooded homogeneous mathematical model that simulated the impedance spectra and the model was validated by the ECE-Damjanovic mechanism on Pt nanoparticles inside Nafion® (similar to the mechanism widely accepted on bulk Pt in acidic medium).

Makharia et al. [10] have obtained inductive loops at low frequencies (down to 0.01 Hz) in Nyquist diagrams with H_2/O_2 experimental method, which characterizes the cathode catalyst layer (CL), but they did not elaborate the causes of this phenomena,