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Nonlinear frequency response analysis of PEM fuel cells for diagnosis of dehydration, flooding and CO-poisoning

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ABSTRACT

Membrane dehydration, fuel cell flooding and anode catalyst poisoning by carbon monoxide are diagnosed in a single polymer electrolyte fuel cell (PEMFC) using nonlinear frequency response analysis (NFRA). A sinusoidal perturbation of high amplitude is applied to the fuel cell current and the resulting voltage is analysed using the concept of higher order frequency response functions. It is shown that the linear part of the system response corresponds to classical Electrochemical Impedance Spectra (EIS), which are not sufficient to clearly distinguish between different fuel cell failures. Therefore, the nonlinear behaviour is additionally taken into account in the form of the second order frequency response function. With this, it is possible to distinguish unambiguously between the three analysed PEM fuel cell failures.

1. Introduction

Sustainable and ecological energy production is one of the major issues of mankind [1]. One possible solution for an effective and sustainable energy conversion is the fuel cell technology, because here chemical energy is directly converted into electrical energy. Especially proton exchange membrane fuel cells (PEMFCs) have been extensively developed in the past decade and manufacturers are working on applying hydrogen and fuel cell technology within their products.

Practical, economical and environmentally friendly sources for fueling PEMFCs are reformate gases from a variety of hydrocarbons (e.g. biogas, methane, gasification of renewable resources) and alcohols (e.g. methanol, ethanol). One major drawback is that reformate gas contains substantial amounts of carbon monoxide (CO) which reduces the catalytic activity of the platinum catalyst in the fuel cell [2,3]. By preferential oxidation it is possible to reduce the amount of CO down to several 10 ppm, but transient peaks of CO can poison the catalyst and reduce the performance of the fuel cell considerably.

Additionally, several other problems leading to performance loss have to be resolved. For example, water management has a major impact on the PEMFC performance [4–8]. While dehumidification leads to drying of the membrane [9,10], excess water causes flooding of the gas diffusion and catalyst layers [9,11,12].

For the diagnosis of these fuel cell failures, Electrochemical Impedance Spectroscopy (EIS) is a well established method [9,12–16]. This method is based on a small sinusoidal perturbation of the electrochemical system (either in current or voltage) and measuring the response signal. Because of the small amplitude of the perturbation, the system is assumed to be linear in the range of the perturbation and the linear impedance is analysed. Due to the variation of the perturbation frequency, processes with different time constants can be separated. With this, EIS has been applied for the analysis of dehydration and flooding [10,12,17–19] and CO-poisoning [20–23]. Nevertheless, some deficiencies of the method have been found. Impedance spectra for different processes can be similar, like for flooding and CO-poisoning under certain operation conditions [15]. This is the case if the processes have similar time constants and therefore are measured in the same frequency range. Additionally, a masking effect due to the high double layer capacity can occur. This made it impossible, e.g. to distinguish between thin film diffusion and agglomerate diffusion of oxygen at the cathode [13,24]. Another drawback of EIS is that for the complete characterisation of the nonlinear fuel cell behaviour multiple impedance spectra at various working points would be necessary.

In classical EIS, small amplitudes are applied to the system and the quasi-stationary response is measured. In the present analysis higher amplitudes are used, which produce nonlinear distortions of the response. The Nonlinear Frequency Response Analysis (NFRA) is, along with other methods, a qualified frame for the analysis of

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the nonlinear behaviour. The aim of this study was to distinguish confidently between the PEMFC failures dehydration, flooding and CO-poisoning, which is not possible with classical EIS. Therefore, in contrast to classical EIS the fuel cell was excited with large amplitudes and higher order frequency response functions (HFRF) were used for the mathematical treatment of the fuel cell response. This concept is based on Volterra series and multidimensional Fourier transforms. It has been developed and applied to electrical systems [25] and effectively used to analyse mechanical systems [26] and chemical process systems [27–29]. It was introduced into the field of electrochemistry very recently by a theoretical work of Bensmann et al. [30].

2. Mathematical background

There are several approaches to analyse nonlinear systems in the literature. A well established method in the electrochemical field is high amplitude AC voltammetry, especially developed in the group of Alan Bond and co-workers [31]. In the field of corrosion the group of Hubin et al. uses specially designed broadband excitation signals to determine impedance, the level of the disturbing noise, the level of the nonlinear distortions, and the level of the non-stationary behaviour simultaneously [32,33]. Another nonlinear method descended from EIS is the so called Nonlinear Electrochemical Impedance Spectroscopy (NLEIS), suggested by Darowicki and co-workers in the field of corrosion [34]. The group of Adler and co-workers used NLEIS successfully for the investigation of solid oxide fuel cell cathode materials [35,36]. In their work, measurements at 10 different amplitudes are fitted to a power series, which describes the nonlinearities of the system.

The present mathematical treatment results in similar functions as obtained by the group of Adler, but with measurements at only one carefully selected amplitude. A detailed comparison of both methods can be found in Bensmann et al. [30].

The concept of NFRA, employed in this study, can be applied to weakly nonlinear systems. The response $y(t)$ of a nonlinear system with polynomial nonlinearity to any input $x(t)$ can be represented by the Volterra series [37]:

$$y(t) = \sum_{n=1}^{\infty} \underbrace{\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty}}_{n\text{-fold}} h_n(\tau_1, \ldots, \tau_n) x(t-\tau_1) \ldots x(t-\tau_n) d\tau_1 \ldots d\tau_n \tag{1}$$

The function $h_n(\tau_1, \ldots, \tau_n)$ is the generalised impulse response function of order n, also known as the nth order Volterra kernel. The application of the multidimensional Fourier transform to this function [25], provides the higher (nth) order frequency response function (FRF) $H_n(\omega_1, \ldots, \omega_n)$:

$$H_n(\omega_1, \ldots, \omega_n) = \underbrace{\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty}}_{n-fold} h_n(\tau_1, \ldots, \tau_n) e^{-j(\omega_1\tau_1 + \ldots + \omega_n\tau_n)} d\tau_1 \ldots d\tau_n \tag{2}$$

For $n = 1, h_n$ is the linear impulse response function and H_n is the linear frequency response function, which corresponds to the classical EIS spectrum. The frequency response functions of higher orders describe the nonlinearity of the system and are therefore able to provide information which cannot be obtained from EIS.

If the input to the nonlinear system is a single harmonic function of the form:

$$x(t) = A\cos(\omega t) = \frac{A}{2}e^{j\omega t} + \frac{A}{2}e^{-j\omega t} \tag{3}$$

the first three elements of the Volterra series (1) are as follows:

$$\begin{aligned} y(t) = {} & \left(\frac{A}{2}\right)e^{j\omega t}H_1(\omega) + \left(\frac{A}{2}\right)e^{-j\omega t}H_1(-\omega) + \left(\frac{A}{2}\right)^2 e^{2j\omega t}H_2(\omega,\omega) \\ & + 2\left(\frac{A}{2}\right)^2 e^{0}H_2(\omega,-\omega) + \left(\frac{A}{2}\right)^2 e^{-2j\omega t}H_2(-\omega,-\omega) \\ & + \left(\frac{A}{2}\right)^3 e^{3j\omega t}H_3(\omega,\omega,\omega) + 3\left(\frac{A}{2}\right)^3 e^{j\omega t}H_3(\omega,\omega,-\omega) \\ & + 3\left(\frac{A}{2}\right)^3 e^{-j\omega t}H_3(\omega,-\omega,-\omega) + \left(\frac{A}{2}\right)^3 e^{-3j\omega t}H_3(-\omega,-\omega,-\omega) + \ldots \end{aligned} \tag{4}$$

With this mathematical background it is possible to analyse any weakly nonlinear system with a polynomial nonlinearity. The Volterra kernels $H_n(\omega_1, \ldots, \omega_n)$ can be derived analytically from a nonlinear model, experimentally as in the present work or from numerical simulations. The comparison of analytically derived kernels with kernels gained from experiments can be used to discriminate or validate a nonlinear model of an electrochemical system, as shown by Bensmann et al. [30] or to estimate unknown system parameters. If an analytical solution of the nonlinear model is not possible or too complex, the numerically simulated kernels of the model can be compared to the kernels gained from experiments to find patterns which may be sufficient for diagnosis of the system.

The determination of the Volterra kernels from experimental data or numerical simulations can be demonstrated by adding some further elements of the Volterra series to Eq. (4) and rearranging of the resulting relation. Sorted by the power of $e^{j\omega t}$ it reads:

$$\begin{aligned} y(t) = {} & e^0\left[\underbrace{\frac{A^2}{2}H_2(\omega,-\omega) + \frac{3}{8}A^4H_4(\omega,\omega,-\omega,-\omega) + \ldots}_{H_{q,DC}(\omega,A)}\right] + \frac{1}{2}\left(e^{j\omega t}\left[\underbrace{AH_1(\omega) + \frac{3}{4}A^3H_3(\omega,\omega,-\omega) + \ldots}_{H_{q,I}(\omega,A)}\right]\right. \\ & + e^{-j\omega t}\left[\underbrace{AH_1(-\omega) + \frac{3}{4}A^3H_3(\omega,-\omega,-\omega) + \ldots}_{H_{q,I}(-\omega,A)}\right] + e^{2j\omega t}\left[\underbrace{\frac{A^2}{2}H_2(\omega,\omega) + \frac{A^4}{2}H_4(\omega,\omega,-\omega,-\omega) + \ldots}_{H_{q,II}(\omega,A)}\right] \\ & + e^{-2j\omega t}\left[\underbrace{\frac{A^2}{2}H_2(-\omega,-\omega) + \frac{A^4}{2}H_4(\omega,-\omega,-\omega,-\omega) + \ldots}_{H_{q,II}(-\omega,A)}\right] + e^{3j\omega t}\left[\underbrace{\frac{A^3}{4}H_3(\omega,\omega,\omega) + \frac{5}{16}A^5H_5(\omega,\omega,\omega,\omega,-\omega) + \ldots}_{H_{q,III}(\omega,A)}\right] \\ & \left. + e^{-3j\omega t}\left[\underbrace{\frac{A^3}{4}H_3(-\omega,-\omega,-\omega) + \frac{5}{16}A^5H_5(\omega,-\omega,-\omega,-\omega,-\omega) + \ldots}_{H_{q,III}(-\omega,A)}\right]\right) + \ldots \end{aligned} \tag{5}$$