Detection of Membrane Drying at Electrochemical Hydrogen Compressor

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ABSTRACT: *Electrochemical hydrogen pump (EIIP) is capable of extracting hydrogen from miscellaneous gases and compress it to very high pressures. Since during its operation it does not produce water the performance is heavily dependent on humidity of the membrane. Online humidity estimation is performed by means of performing electrochemical impedance spectroscopy (EIS).*

Keywords: EIIP, EIS, Wavelets, Impedance, DRBS

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1. Introduction

Renewable energy sources such as wind turbine farms and solar power plants are ubiquitous in our energy systems. Despite their indisputable positive environmental impact, their main drawback is the intermittent power output. In many cases, the generated energy has a significant mismatch to the demand on the grid. For that reason the need for energy storage installations, that are capable of storing vast amounts of energy in times of surplus while being capable for instant on-demand delivery is of a great importance. Currently there are two competing technologies that are addressing these issues: batteries and fuel cells. Our focus in this paper will be on the latter.

Fuel cells operate on the chemical energy stored in form of hydrogen molecules. Hydrogen is one of the most abundant elements and has great properties of being an energy-rich gas and highly versatile. This makes hydrogen as one of the most suitable candidate to be used as an efficient energy storage media [1, 2]. Compressing the hydrogen to high pressures while maintaining high purity is a challenging process and consumes a lot of energy. There are two general categories of hydrogen compressors: mechanical, which uses adiabatic process and non-mechanical, which mainly uses isothermal process for compression.

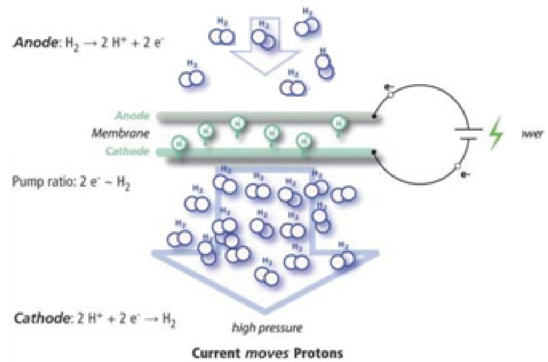

Figure 1. Basic operational concept of how EHP works. I uses an external voltage source to efficiently pull only hydrogen protons through the proton conductive membrane [4]

Non-mechanical compressors such as electrochemical hydrogen pumps (EHP) uses electricity to extract hydrogen from miscellaneous gas mixtures and compress it in order to meet different application requirements. The lack of moving parts makes them more efficient when compared to the conventional mechanical compressors which are noisy, can induce impurities and less effective [3]. The structure of EHP is similar to that of a Proton Exchange Membrane Fuel Cells (PEMFC). The basic principles about how EHP works are shown in the Fig. 1.

Hydrogen molecules enter the anode side (the low pressure side) where are oxidised to protons and electrons. The applied voltage force the electrons through an external circuit while the protons are driven through the membrane to the cathode side where are recombined to form again a molecular hydrogen. As a result of the external voltage, the pressure at the cathode side increases with the increased number of transported hydrogen molecules.

Despite EHP advantages, they have mainly been used as a diagnostics test for measuring crossover in fuel cells. Ströbel et al. [5] was the first one to recognize the possibilities of the PEM-based structure for EHP. Hao et al. [6] performed electrochemical impedance spectroscopy (EIS) on EHP with included internal humidifier with dead-end anode. Nguyen et al. [7] has shown how the temperatures of the humidifier and the temperature of the stack are influencing the performance of the stack. From the previous reported analysis, they all address the problem of controlling the humidity of the membrane, which is essential for the transportation of protons through the membrane and is tightly connected to the overall performance of the EHP. On the other hand, shortage of humidity reduces the proton conductance. Due to the fact that EHP does not produce water, when compared to the PEM fuel cells, it has to be delivered via an external humidifier.

Online monitoring the level of humidity of the membrane by performing direct measurements is almost impossible due to the physical inaccessibility of the membrane. The only possible way to perform online estimation of the humidity is by performing an EIS. Classical way of performing EIS includes single sine excitation signals. As a result of this the characterisation process is often time consuming and lacks of accuracy especially in the low frequency region, which can be crucial and reduce the applicability for online applications. Using stochastic excitation, for instance discrete random binary sequence (DRBS), alleviates the aforementioned problems. This method has successfully been tested on PEM fuel cell [8]. For the purpose of this paper two experiments were performed, one in normal operating mode when the membrane was well humidified and an other when EHP was operating in drying mode. The experiments were performed in the frequency band between 0.1 Hz and 1000 Hz.

2. Wavelet Transform For Impedance Calculation

The conventional frequency domain signal analysis performed with the Fourier transform, provides a detailed picture of the frequency components present in the signal but without any information regarding their time occurrence and duration. Time-frequency analysis offers a solution to this problem thus providing the information about the temporal details as well. Typical examples are the Short-time Fourier transform, Wigner-Ville distribution, wavelet transform etc.

Regardless of the selected method there is a theoretical limitation on the joined time-frequency resolution. Unlike other methods, the wavelet transform enables flexible selection of the desired time-frequency resolution by introducing the concepts of scaling. Wavelet transform is based on a set of specifically designed functions called wavelets. The continuous wavelet transform (CWT) of a square integrable function $f(t) \in L^2(\mathbb{R})$ is defined as [9]:

$$Wf(s,u) = \int_{-\infty}^{\infty} f(t)\psi_{u,s}^{*}(t)dt$$

where wavelet function $\psi(t)$ is scaled and translated by introducing two additional parameters u and s:

$$\psi_{u,s}(t) = \frac{1}{\sqrt{s}}\psi\left(\frac{t-u}{s}\right)$$

The key parameter in *CWT* is the selection of the wavelet function. *EIS* analysis requires information about the amplitude and phase of the excitation and response signals. Therefore, the *CWT* is performed with a complex wavelet function, in our case the Morlet wavelet[10]:

$$\psi(t) = \pi^{-\frac{1}{4}}\left(e^{-j\omega_0 t} - e^{-\frac{\omega_0}{2}}\right)e^{-\frac{t^2}{2}}$$

where ω_o is the central frequency, whose value is linked to the time-frequency resolution of the wavelet. The link between the Morlet wavelet's scale parameter s and the actual frequency is through the following relation:

$$\frac{1}{f} = \frac{4\pi s}{\omega_0 + \sqrt{2+\omega_0^2}}$$

The time and frequency localisation is determined through the parameters u and s respectively. The scale parameter s acts as a dilatation factor of the mother wavelet, which determines the frequency region of the wavelet analysis. The translation parameter u defines a time location where the instantaneous phase and amplitude are estimated. More details regarding the properties of the Morlet wavelet and the application of CWT for EIS analysis can be found in [11, 12].

3. Experiment Setup

An experimental environment was established in order to perform diagnostic experiments on 5 cell EHP stack. All connections, pipings and instrumentations are shown in Figure 2.

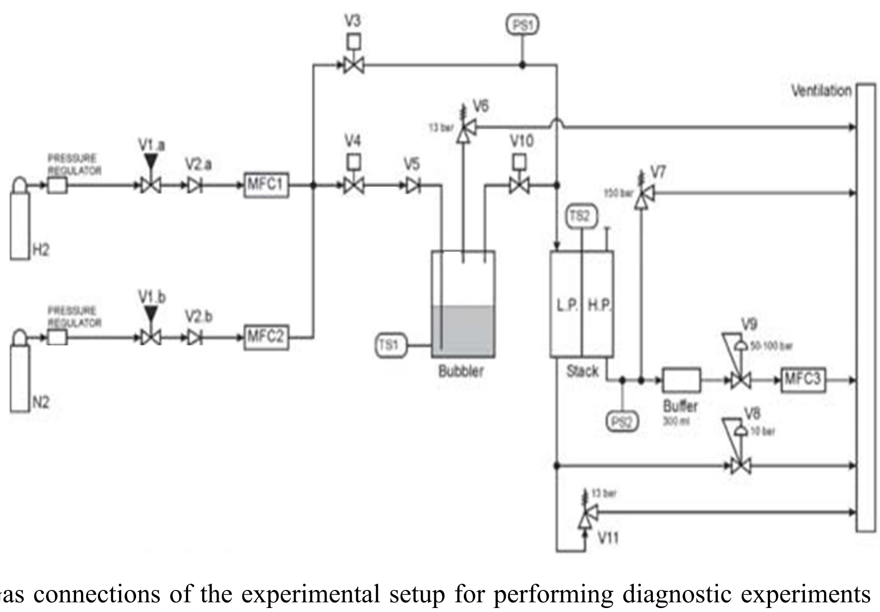

Figure 2. Gas connections of the experimental setup for performing diagnostic experiments on EHP

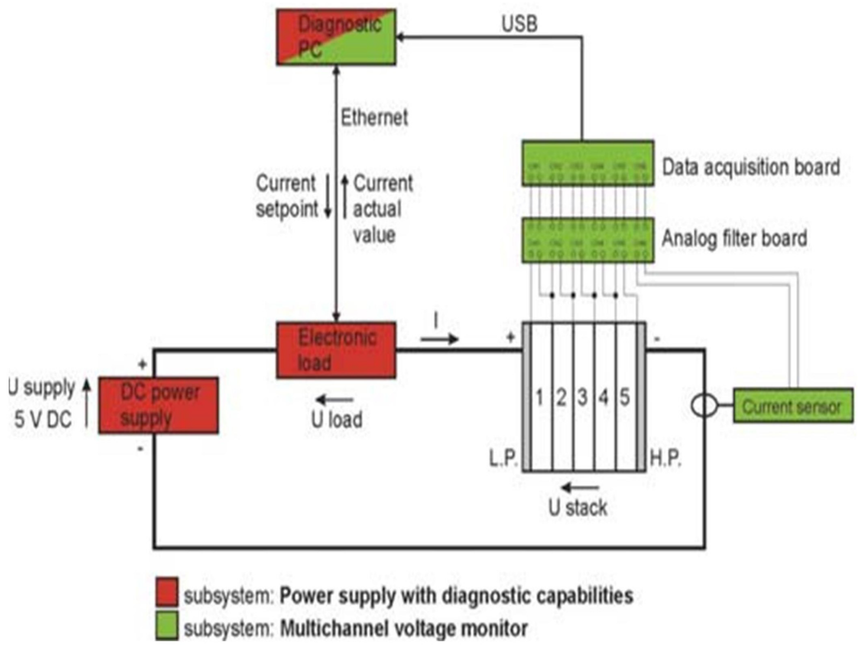

Figure 3. Electrical connection of the EHP for performing electrochemical impedance spectroscopy

From the Figure 2 mass flow controller MFC1 is used to supply hydrogen to the stack, while MFC2 is used to supply the "impurity", for example nitrogen. Solenoid valve V3 is used to deliver the hydrogen mixture to the stack directly, without humidification, while valves V4 and V10 deliver the hydrogen mixture to the stack through the humidifier (bubbler). Backpressure regulator V8 controls the pressure at the low pressure side of the stack. On the high pressure side there is a buffer to accumulate the pumped hydrogen and back pressure regulator V9 to control the pressure in the tank and at the high pressure side of the stack at constant value. Mass flow controller MFC3 is used as a mass flow meter to measure the output flow rate. In steady state, MFC3 reading equals the hydrogen flow rate from the high pressure side of the stack.

Electrical connections on the EHP, which are essential to perform diagnostics, are shown in the Fig. 3. Characterization of the cells is performed at *DC* currents I_{DC} = 20 A with peak-to-peak amplitude I_{AC} = 1*A* by using classical single sine wave and stochastic DRBS excitations. The perturbed current is induced using programmable digital electric load (Rigol DL3031A) with excitation frequencies starting from 0.1 Hz up to 1000 Hz. The voltage response of the cells together with the current are sampled with sampling frequency f_s = 50 kHz using 16-bit data acquisition card (NI USB 6215). Before DAQ signals are low pass filtered at f_c = 10.8 kHz.

All controllable variables are kept constant during the process of characterization. Due to the fact that we were not able to directly measure and to give a precise quantification of the humidity level of the membrane, the first experiment was performed at nominal conditions with the humidifier (bubbler) and the second experiment was performed when the humidifier was turned off.

4. Results

In order to perform EIS, operating condition of the EHP must fulfil the linearity conditions, which are tightly connected to the amplitude of the excitation signal. Therefore, the excitation amplitude must be small enough in order to operate within the linear region but big enough to measure its response.

Before performing an EIS characterisation, the IV curve of the cell was first measured in order to determine the AC amplitude at desired DC current. From the IV curve (Fig. 4) it was decided to perform the EIS characterisation at I_{DC} = 20A with peak-to-peak amplitude I_{AC} = 1 A using *sine wave* and *DRBS* excitation signals.

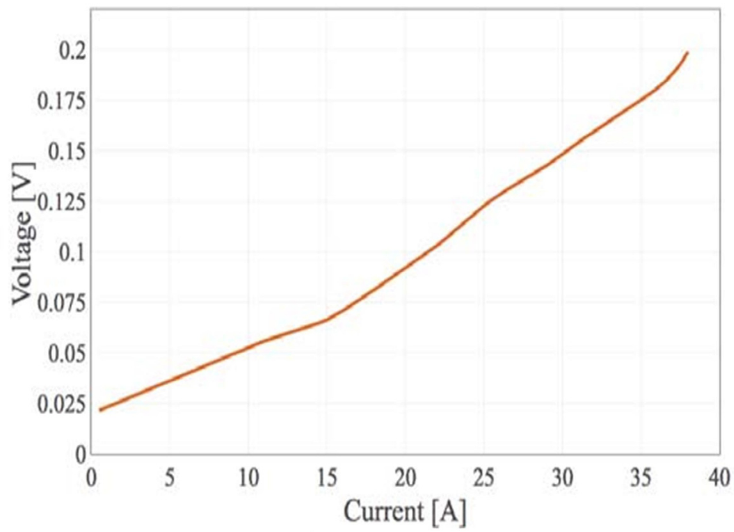

Figure 4. IV curve of the 2nd cell from the HyET electrochemical hydrogen pump

The impedance of the cell under a test was first calculated using single sine wave excitation signals. It was calculated at 20 different frequency pints starting from 0.1 Hz up to 900 Hz (5 points per decade). In order to have good calculation of the impedance at every frequency point, at least 10 cycles are needed in order to obtain good quality of the acquired signal. For that reason, the excitation time at 0.1 Hz is 100 seconds.

Following this, the time needed to calculate the impedance at 20 different frequency points is almost 200 seconds.

By using DRBS as excitation signal (Fig. 5) the time needed for characterization is only 110 seconds, which represents 45 % decrease in time when compared to the classical sine wave excitation method. However, the main advantage of this method would be the ability to calculate the impedance in desired number of frequency points. In Fig. 6 is shown the comparison between the impedances calculated using sine wave and DRBS excitation signals. From the figure it can be concluded that the impedance calculated using DRBS is almost the same as the impedance calculated using classical single sine wave. The only difference would be in the low frequency region (at 0.1 Hz). The reason for this behaviour is due to the small changes in the operating point caused by stack temperature fluctuation.

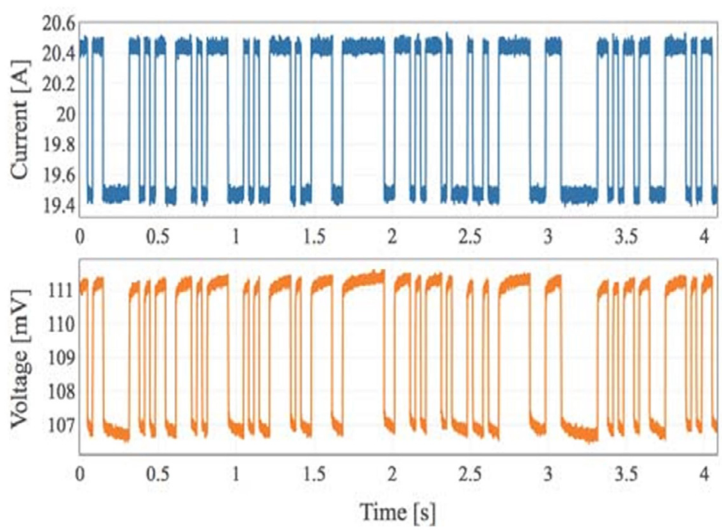

Figure 5. DRBS current excitation signal and the voltage response of the cell

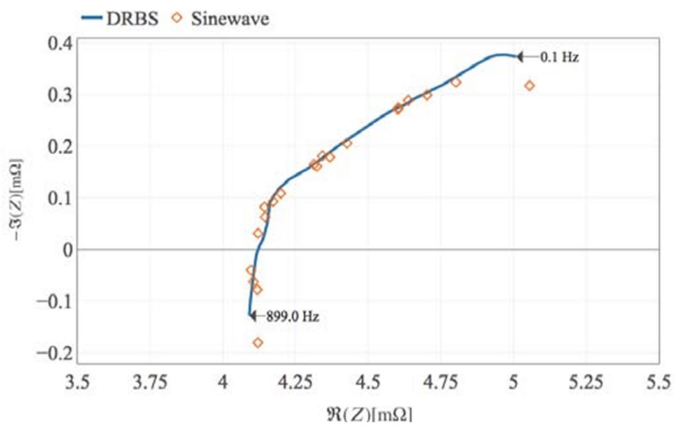

Figure 6. Comparison between impedances calculated using classical single sine and DRBS excitation signal

In Figure 7 is shown how the impedance changes when the cell operates in normal operating mode and in drying mode. From the shape of the impedances it can be concluded that drying operation mode causes a right shift and swelling. This behaviour is caused due to increase of the resistivity, which is connected to the size of the water clusters within the polymer microstructure. Dehydration of the EHP membranes leads to narrowing of the interconnecting channels which decreases the 1 mobility of the protons and increases the electrical resistance [13]. Since calculation of the impedance using DRBS signals takes less time, it is more suitable for performing online monitoring of the humidity of the membrane inside the EHP.

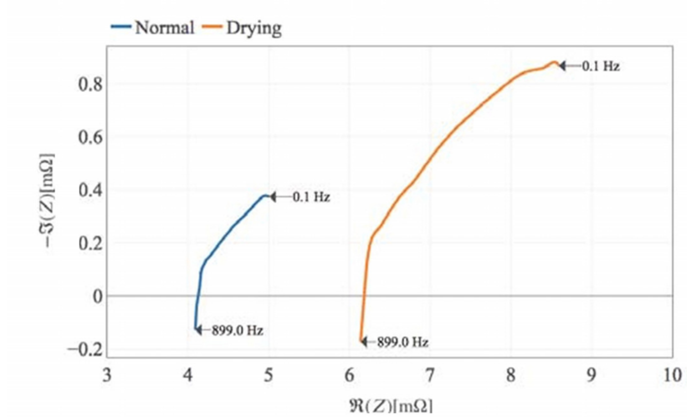

Figure 7. Impedance of the cell at normal and drying operating conditions

4. Conclusion

Monitoring the level of humidity inside the membrane is crucial for maintaining its performances. Performing direct measurements of the humidity of the membrane is almost impossible due to the physical limitations. The only possible way is by using electrochemical impedance spectroscopy.

Impedance of the EHP was measured in the frequency interval between 0.1 Hz and 900 Hz using classical single sine and DRBS excitation signals at two different operating modes *normal* and *drying*. Classical way of performing EIS, which included calculation of the impedance in 20 different frequency points. Despite the accuracy of the calculation, classical way is usually time consuming and lack of accuracy especially in the low frequency region. By using stochastic excitation (DRBS) combined with wavelet transform, the impedance can be calculated in in desired number of frequency points. In addition to this, the time needed for characterization, when compared to the classical way, was decreased by almost 45 %. Therefore, performing EIS by using DRBS excitation signals is more adequate method for monitoring the level of humidity of the membrane.

From the obtained impedances can be seen that drying shifts the impedance to the right, which is directly connected to the increase of the membrane impedance. From this we can assume that by monitoring how the impedance is shifting it is possible to measure the humidity of the membrane while in operating mode.

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