Materials Science and Engineering, Volume 40, No. 1 (2015) pp. 56–63.

TRIANGULAR AND SQUARE VOLTAGE WAVEFORMS IN WATER ELECTROLYSIS – INFLUENCE OF FREQUENCY AND AMPLITUDE CHANGE

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Alkaline water electrolysis is a traditional way of hydrogen generation. Water splitting via the use of direct current is a well-known process, however alternating, fluctuating or impulse current is one of the hot research topics today. Using direct current no gas release is observed on electrodes until voltages of 1.65–1.70 V are applied, but if the voltage between the electrodes is fluctuating, the average voltage can be less than the mentioned limit. The main goal of this study is to showhow the cell power, the generated gas flow rate and the efficiency is affected by fluctuating voltage around the 1.48 V isothermal operation. Square and triangular waveforms were applied to the cell with an average voltage of 1.5 V. The frequency and the amplitude of the waveforms was changed from 1 Hz to 99 Hz and from 0.1 V to 3.9 V with a resolution of 2 Hz and 0.2 V. Thus 2000 individual measurements were made by an automatic measurement system designed for the alkaline water splitting.

Keywords: water electrolysis, voltage waveform, electrolysis efficiency

Introduction

Hydrogen generation by water splitting theoretically requires potential difference of 1.23 V between the electrodes at temperature 298 K and ambient pressure (reversible voltage) [1, 2]. However, hydrogen generation using less than 1.48 V is possible only if heat is absorbed while heat must be supplied for the process to work above 1.48 V (thermoneutral voltage) [2, 3, 4]. The mentioned thresholds are temperature dependent (Figure 1) [4]. Practically no gas generation is observed until 1.65–1.70 V is applied, and the commercial water electrolyzers are operating with 1.8–2.6 V because of intentional overvoltages and the necessary ohmic losses [4, 5].

Efficiency of water electrolysis depends on many factors including the waveform of the applied voltage. Although there are several papers about applying impulse voltage or interrupted direct current to the cell [6, 7, 8, 9], some authors says that the amount of available papers in this area is low, and more experimental studies are required [10, 11], probably because of the following reason: the waveform parameters, such as frequency, amplitude, offset and waveform type can be varied almost independently over a very broad range [12].Our main goal is toselect a subset of the possible settings, and apply two different types of waveforms (square and triangular) to the cell at offset voltage 1.5 V (a value close to the thermoneutral voltage at normal temperature conditions) and to analyze the gas production, the electric power of the cell, and the efficiency of the electrolysis as a function of frequency and amplitude.

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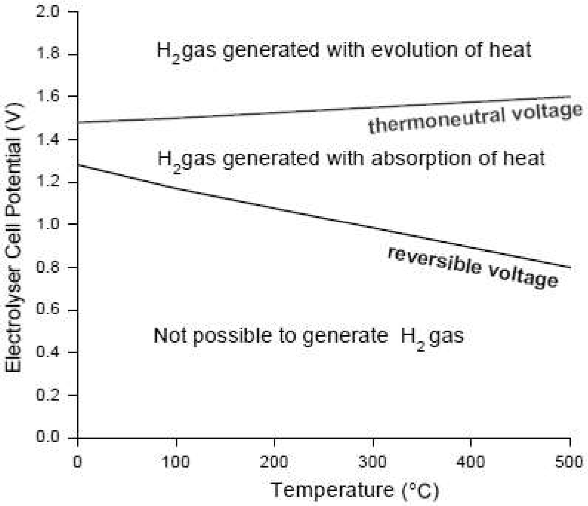


Figure 1. Hydrogen generation by water electrolysis as a function of temperature

1. Measurement system overview

Figure 2 illustrates the block diagram of the measurement system. The main component is the gas-tight cell powered by a special power supplythat is controlled by a dedicated National Instrumentsdevice (NI USB-6259). Its operation can be automated using a LabVIEW program. The device is responsible for measuring the cell voltage, the cell current and the pressure of the generated gas. It can alsocontrol the electric valve connected to the top of cell.

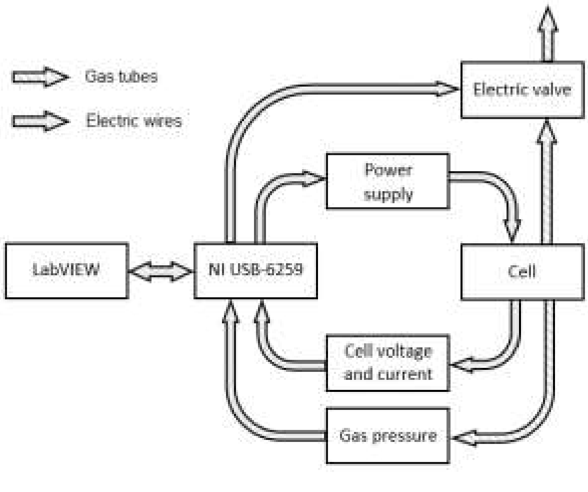


Figure 2. Block diagram of the measurement system

The measurement algorithm was the following:

A) initial parameters (voltage waveform) areset;
B) the actual waveform is applied to the cell for 15 s, while the cell voltage, cell current and the actual pressure of generated gasis recorded at a rate of 4000 samples/s;
C) data collection is stopped and the power supply is turned off;
D) system relax time for 5 s;
E) valve is opened for 4 s so that the produced gas can leave the cell and the pressure can come into equilibrium with the ambient;
F) valve is closed and the system paused for 1 s;
G) frequency and/or the amplitude is adjusted;
H) the procedure is repeated from step B until the system reaches the last frequency and amplitude setup.

The power supply can be operated between –10 V and +10 V. The maximum current is limited to 8 A, and the frequency limit is 50 kHz. The power supply can produce various waveforms within the limits. The frequency and the amplitude of the triangular and square waveforms were changed from 1 Hz to 99 Hz and 0.1 V to 3.9 V, respectively, with frequency resolution of 2 Hz and amplitude resolution of 0.2 V. Thus2000 individual measurement were performed.The measured data points were logged in separate files.Manual evaluationof each file would have been a long process, thus a special data estimator software was created in the programming language C#. The software computes the two main parameter of each measurement: the pressure and the cell power change with time. The velocity of increase in gas pressure is proportional to the gas flow rate. The exact ratio can be determined by calibration.

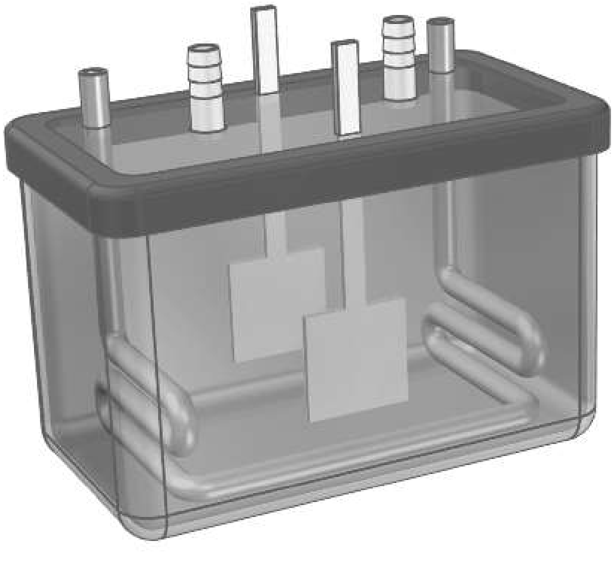


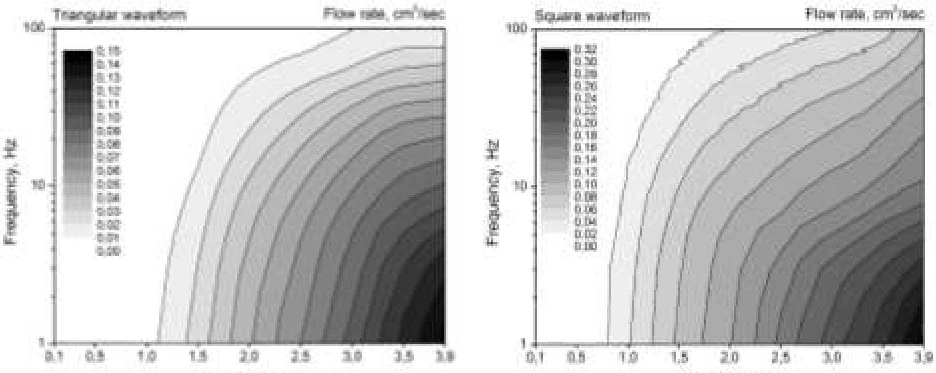
Figure 3. The cell used for water electrolysis

The sketch drawing of the cell is shown in Figure 3. The electrode was made of stainless steel with cross sections of 25 mm x 25 mm, and with thickness 1.5 mm (material type: 1.4307). The distance between electrodes was adjusted to 40 mm. 1 mol/l KOH solution was used as electrolyte with volume 500 ml. The cell contains two gas outlets. One of them was connected to pressure sensor (type: MPX5010DP), the other to an electrically controllable valve. The cell also contains a water-cooling circle in order to keep the electrolyte temperature at constant value. The temperature was measured by T-type thermocouple inserted into the electrolyte and connected to a temperature meter. The typical electrolyte temperature was 25 ±1 °C for each measurements.

2. Results

The generated gas flow rates as a function of frequency and amplitude are shown in Figure 4a (triangular waveform) and 4b (square waveform), respectively. The trends in both cases are similar: while the frequency increases or the amplitude decreases the gas flow rate decreases.The graphs also show, that by increasing the frequency the gas flow rate sooner or later reaches a frequency limit.Oncethe frequency is over the limit the gas flow rate equals to flow rate measured in DC case with the samevoltage as the waveform offset (while the power consumption is still increasing with increasing frequency).Because there was no gas flow at 1.5 VDC, the gas flow rate at frequencies greater than the frequency limit is also zero. The frequency limit depends on many factors, at least on amplitude, offset, and voltage waveform. The statement is supported by prior measurements at different offset voltages ranging from 1 V to 3.5 V.

Behaviour of the increasing amplitude is somewhat different. Above an amplitude limit the gas flow rate starts to increase, while the average voltage of the waveform is still 1.5 V. The smallest amplitude limit was at square waveform approximately0.7 V at frequency 1 Hz.



a) b)

Figure 4. Flow rates: Frequency and amplitude dependence for triangular and square waveforms

The square waveform generates at least 1.8 times more gas than the triangular waveform, but the exact square/triangular flow rate ratio depends on frequency and amplitude (Figure 5). The graph shows that the ratio is increasing while the amplitude is decreasing, and at low frequencies the difference between the ratios at various amplitudes is smaller. The results shown on graph are polynomial type regressions on data points. The minimum value of the coefficient of regression (R^2) in each case is 0.97, the only exception is the 1.1 V line, where $R^2 = 0.88$.

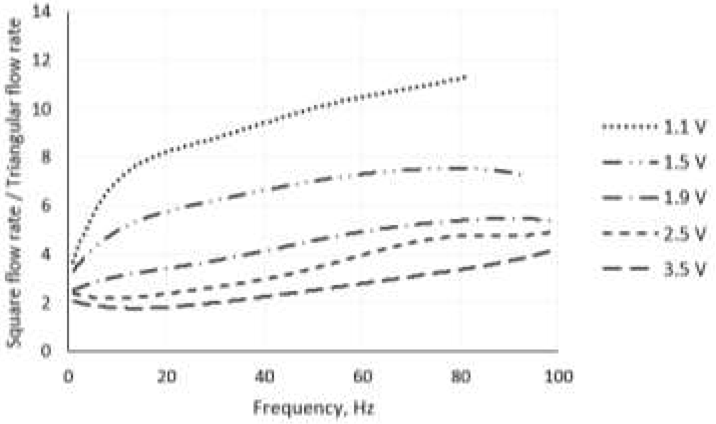


Figure 5. Square/Triangular flow rate ratio as a function of frequency and amplitude

Figure 6 illustrates the cell power as a function of frequency and amplitude using triangular and square waveforms, respectively.The results of both waveforms are similar: increasing the frequency and/or the amplitude also increases the cell power. However, the power measured with square waveform is much higher than the power measured with triangular waveform at the same settings.

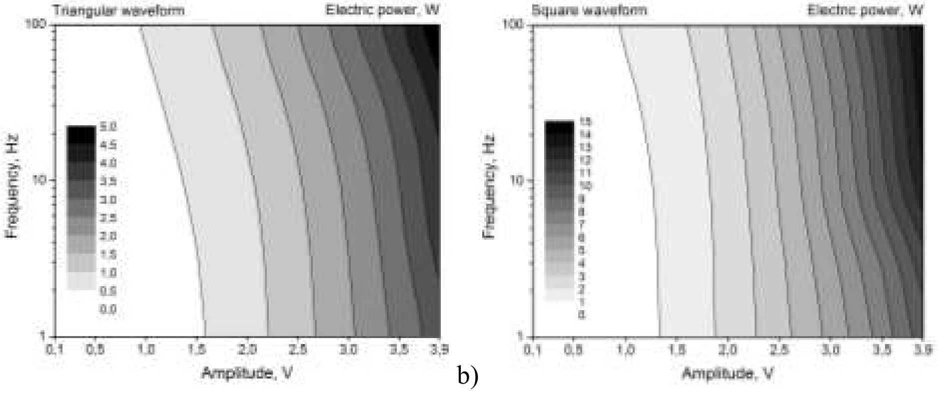


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Figure 6. Cell power: Frequency and amplitude dependence for triangular and square waveforms

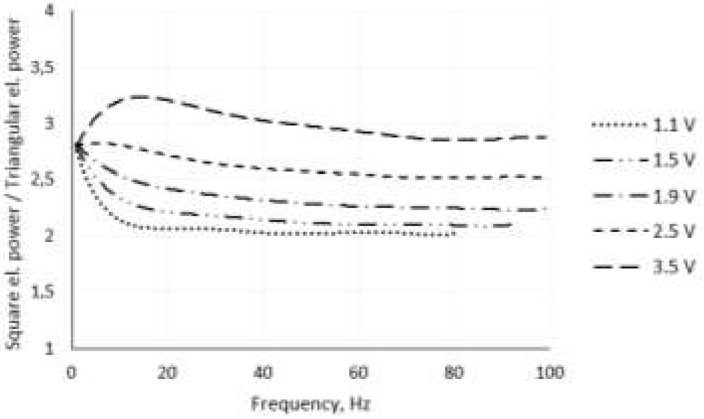

Figure 7. Square/Triangular power ratio as a function of frequency and amplitude

Figure 7 illustrates the exact square/triangular cell power ratio. The trends are somewhat different than the flow rate ratio. The curves on graph have a commonintersection at frequency 1 Hz and around ratio 2.8.

The cell efficiencies as a function of frequency and amplitude using triangular and square waveforms, respectively, are shown in Figure8. The efficiency was computed from flow rates and cell powers. Ideal gas flow rate (V_i) was calculated for each cell power values [5], and with the help of the real (measured) gas flow rate (V_m), the efficiency was calculated by the following equation [5]:

$$\eta = \frac{V_i}{V_m} \cdot 100$$

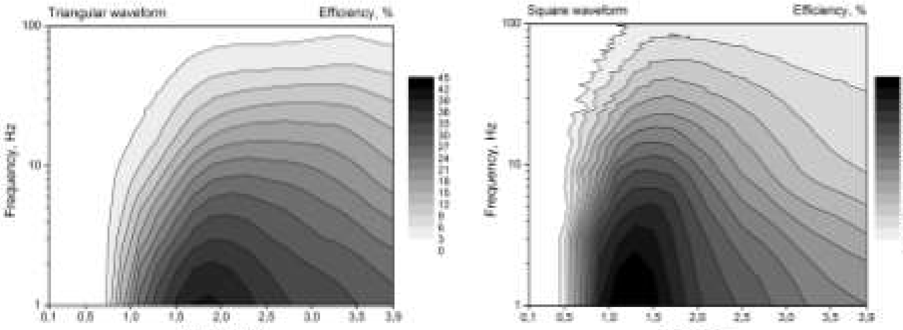

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Figure 8. Cell efficiency: Frequency and amplitude dependence for triangular and square waveforms

The maximum efficiency using square waveform was at amplitude 1.3 V while it was 1.8 V for triangular waveform. The figures show, that by applying 1.5 V DC (0 V amplitude would mean DC) to the cell the efficiency is practically zero, however with increasing the amplitude the efficiency starts to increase but bear in mind, that the average voltage (offset) is still 1.5 V. A value higher than 1.5 V in amplitude means, that the polarity of the electrodes is always changing, but there are no obvious signs of this effect in efficiency, flow rate or cell power graphs.

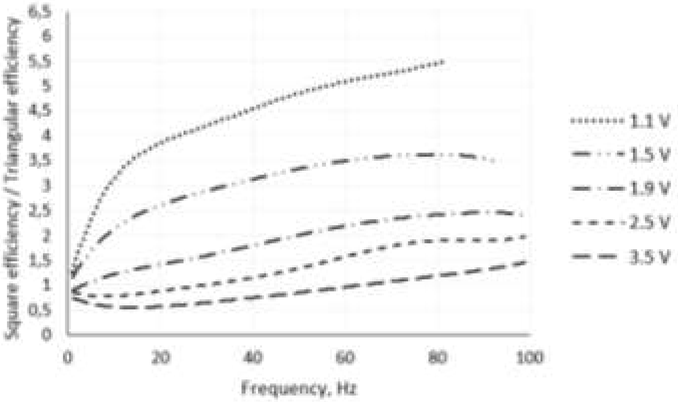

Figure 9. Square/Triangular efficiency ratio as a function of frequency and amplitude

Figure 9 illustrates the efficiency ratio of two waveforms. While the flow rate and cell power using square waveform was always greater, the efficiency ratio at some settings is less than 1. At high amplitude and low frequency settings the efficiency of water electrolysis is greater by applying triangular waveform to the cell, but at low amplitudes and high frequencies the square waveform is better.

Summary

The gas flow rate and the cell power of water electrolysiswere measured. Square and triangular waveforms at different frequencies and amplitudes were applied to the cell at a fixed 1.5 V offset. The efficiency of the system was computed from the gas flow rate and cell power.

It was shown that the produced H_2+O_2 gas flow rate is increasing with increasing amplitudes and decreasing frequencies. The maximum efficiency of the electrolysis process was found at the amplitude of 1.3 V for square and 1.8 V for triangular waveforms, both at 1 Hz frequency. Using the same frequency and amplitude setting at both waveforms, the absolute values of flow rates and cell powers differ significantly.

The high amount of individualdata required the development of an autonomous measurement system where the voltage, current and pressure in the cell are measured and registered according to the control algorithms.

Acknowledgement

This research was realized in the frames of TÁMOP 4.2.4. A/2-11-1-2012-0001 „National Excellence Program – Elaborating and operating an inland student and researcher personal support system convergence program" The project was subsidized by the European Union and co-financed by the European Social Fund. This research was carried out in the framework of the Center of Excellence of Sustainable Resource Management at the University of Miskolc.

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