Water Electrolysis and Pulsed Direct Current

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The potential of hydrogen for playing an important role in future energy systems has led researchers to investigate methods of reducing hydrogen production costs to levels that can compete with petroleum products. One of these methods is the application of pulsed direct current (dc) to a practical electrolysis system, which has generated a considerable amount of interest over the past forty years.

Using a mechanically interrupted dc power supply, Bockris et al. 1-3 reported two phenomena in 1952. Immediately upon the application of potential to an electrolytic cell, a high but short-lived current spike was observed. When the applied potential was disconnected, significant current continued to flow for a short time. They explained the first phenomenon as a double-layer capacitance–charging transient, followed by the electrochemical discharge of the first ionic layer, giving rise to the current, then replenished by the ionic mass transport from the bulk of the electrolyte. The second phenomenon was attributed to ions in the double layer facing the electrode being discharged in the absence of the externally applied field. Their work suggested that the charge and discharge of the double layer may play an important role in reducing power requirements.

In 1984, Ghoroghchian and Bockris 4 designed a homopolar generator to drive an electrolyzer on pulsed dc potential. They concluded that the rate of hydrogen production would be nearly twice as much as the rate for dc. Their conclusion was in agreement with the earlier works of Tseung and Vassie 5 and Jasem and Tseung 6 in these earlier works they attributed the increase in hydrogen and oxygen evolution to an improvement in electrolyzer mass transfer. IbI et al. 7 also has shown that the application of short high-potential pulses yielded the highest possible electrolysis current. He concluded that pulsing affects the surface state of the electrodes. During conventional electrolysis, a film of gas bubbles forms on the electrode, raising its resistance overpotential. Pulsed potential, however, will eliminate the resistance overpotential of the gas bubbles. Ozerov et al. 8 suggested that the rate of electrolysis could be increased indefinitely in pulsed electrolysis by reducing the duration of the pulsed current. Ibl et al. 9 suggested that in the case of short pulses two diffusion layers exist, a pulsating layer near the electrode, and another layer further out, which becomes stationary after a few pulses. Viswanathan et al. 10 showed that the thickness of the pulsating layer is a function of the characteristics of pulsed dc. It was suggested that pulsing action on electrochemical systems could give rise to the ionic vibration potentials. A more drastic effect is to be expected if pulsed power is applied at frequencies resonating with the dominant ionic discharge components. Thus, one of the methods for enhancing the ionic exchange in water electrolysis is the pulsed dc.

The use of pulsed dc for electrochemical reactions, especially in electroplating, is not new. In 1955 Robotron Corporation obtained a patent for high-voltage electroplating using pulsed power. 11 In 1966 Popkov 12 further substantiated the advantage of using pulsed current. Avila and Brown 13 reviewed and confirmed the advantages of pulsed plating on the quality of gold plating for integrated circuitry use while Bockris and Kita 14 obtained a reduction in the energy requirement by a factor of two. Pulsed electrolysis was also used in battery charging by Wagner and Williams 15 and Bedrossian and Cheh. 16

The main objective of the present study is to quantify the effects of pulsed dc on the performance of water electrolysis for hydrogen generation.

**Experimental Setup**

The laboratory setup is shown in Fig. 1, 2, and 3. It consists of an electrolyzer setup as well as pulsed dc power supply sources. The electrolyzer setup includes an electrolytic cell (Fig. 2) model Fm01-LC, rated at 38 g of H₂/kA·h, and manufactured by ICI Chemicals & Polymers Company. The anolyte and catholyte compartments are separated by a du Pont 324-Nafion membrane. The anolyte and the catholyte are pumped through the corresponding compartments so that the anolyte and catholyte are separate except for the ionic exchange through the membrane. The electrolyzer contains a stainless steel cathode and a platinum-coated titanium anode which are placed 3 mm apart. Each electrode has a projected area of 0.64 cm². Throughout the experiment a 10 weight percent (w/o) sulfuric acid solution is used as the electrolyte. The plumbing used to connect the main components are 1.25 cm Teflon pipes, which can withstand a 10 w/o sulfuric acid for temperatures up to 45°C.

The key electronic equipment (Fig. 3) used in this experiment includes the following: Industrial Equipment Company power amplifier, POWERTRAN Model 2000 SHF-1-XX, capable of 0 to ±40 V and 0 to ±120 A with a maximum continuous power output of 2000 W and an amplification factor of 25 (the POWERTRAN was modified to remove the output transformer to allow it to operate from dc to 70 kHz); and a B&K Precision Model 2011B function generator capable of generating square, triangle, and sine waves at frequencies up to 2 MHz with duty cycles ranging from 1 to 99%, and an output amplitude of up to 5 V. The electrolyzer is connected to the power supply by two 0.3 m long No. 4 AWG bare copper wires.

The pressures, temperatures, and flows of the generated hydrogen and oxygen are measured using Ashcroft pressure sensors, 0 to 3.45 x 10⁴ Pascal with ±1% of full-scale accuracy; J-type thermocouples; and Teledyne Hastings-Raydist flowmeters, Model F1MM-200, with a 0 to 500 scm range with ±1% of full scale accuracy and ±0.2% of full scale repeatability. The thermocouples' outputs are conditioned by Validyne TC243 modules with cold junction compensation and 2.5% of full scale gain accuracy. The catholyte and anolyte temperatures are measured by thermometers accurate to ±1°C. The electric current is measured using a F.W. Bell Hall–effect current sensor; Model HHA-100, capable of measuring dc and pulsed current up to 50 kHz, 0 to 100 A with accuracy of ±1% of the measured current.
value. The current is measured in volts, 50 mV being equal to 1 A. Both current and potential are displayed using a Tektronix 2232 100 MHz oscilloscope and then plotted using a Tektronix HC-100 plotter. The plots are digitized using a Summa Sketch II professional digitizer. Potential measurements are taken at the cell and at the power supply output. This allows the measurement of line losses. The pressure, temperature, and flow sensors for hydrogen and oxygen measurements are 60 cm from the point of electrolyte-gas separation in the electrolyte reservoirs. The experimental setup is housed in a fume hood, while the hydrogen line is vented through the wall to the atmosphere and the oxygen line is vented into the laboratory room.

**Laboratory Test Series**

Two sets of tests were carried out. The two test series consisted of: (i) a nonpulsed dc power test set to determine the cell’s base-line performance and (ii) a pulsed dc power test set to determine the cell performance as a function of the pulsed energy parameters. In nonpulsed dc electrolysis, the applied current or potential is varied; whereas in pulsed dc, three parameters can be varied independently. These parameters are the pulse frequency, pulse duty cycle, and potential or current magnitude.

**Base-line test, nonpulsed dc power**—This test series established the performance base-line for the laboratory setup. First, the deactivation of the cell was studied by recording the change in current at fixed potential as a function of time. As shown in Fig. 4, the cell reached steady-state conditions 5 min after potential was applied to the cell. Using this cell property throughout the experiment, data were collected at least 10 min after each test was initiated. The cell’s hydrogen yield as a function of cell potential and current was measured (Fig. 5 and 6) to determine the cell’s base-line performance. The cell’s base-line performance then was used for comparison with cell performance under pulsed dc.

**Pulsed dc power**—For comparison purposes, the hydrogen yield was kept at 100 cm$^3$ for all pulsed dc runs. This selection was determined by the base-line nonpulsed dc current density results. At 100 cm$^3$ of hydrogen (Fig. 6), the measured current density was around 240 mA/cm$^2$ which is in the current-density range of 100 to 500 mA/cm$^2$ for economical hydrogen production. To maintain a hydrogen
generation rate at 100 cm$^3$ for all test runs, the hydrogen temperature and pressure were used to correct flowmeter readings from its standard calibration. The pressure readings stayed at atmospheric pressure while the temperature range fluctuated between 21.3 and 23.8°C, which constitutes a less than 1% change in flow measurements. The test runs were carried out using square pulse for seven frequencies and four duty cycles. The frequency is the ratio of the pulse on-time to the pulse period. The seven frequencies are 0.01 Hz, 0.5 kHz, 5 kHz, 1 kHz, 10 kHz, 25 kHz, and 40 kHz. The duty cycles are 10, 25, 50, and 80%. The test was divided into four test runs, one for each duty cycle. Each test run started by measuring the nonpulsed dc current and potential for a 100 cm$^3$ of hydrogen yield. Then a duty cycle was selected, and the pulse frequency of test run was changed. The cell potential was then changed to maintain about 2.3 V during the off-period of the pulse (Fig. 7). The polarity reversal is attributed to a reversible reaction in the electrolyzer cell during the off-period. The effect of the current polarity reversal was seen in the catholyte when its color changed to a light blue. To examine and quantify the various metals in the catholyte, the atomic absorption spectrometry was used. The observations were made with a Perkin-Elmar 6500 flame atomic absorption spectrometer, using a laminar flame burner and equipped with hollow-cathode emission lamps for the different metals sought. Metals sought were based on the stainless steel alloy, content of the catholyte, the atomic absorption spectrometry was used. Operating at 2.8 V. (n) Measured point.

\[
\begin{align*}
P &= \frac{1}{T} \int_{0}^{T} i(t) \theta(t) dt \\
\theta(t) &= \begin{cases} 
1 & \text{for } 0 < t < T/2 \\
0 & \text{for } T/2 < t < T
\end{cases}
\end{align*}
\]

where $T$ is the pulse period, $i(t)$ is the current waveform, and $\theta(t)$ is the potential waveform.

**Results and Discussion**

During the preliminary test runs, conducted to examine the experiment setup, the current reversed polarity during the off-period of the pulse (Fig. 7). The polarity reversal is attributed to a reversible reaction in the electrolyzer cell during the off-period. The effect of the current polarity reversal was seen in the catholyte when its color changed to a light blue. To examine and quantify the various metals in the catholyte, the atomic absorption spectrometry was used. The observations were made with a Perkin-Elmar 6500 flame atomic absorption spectrometer, using a laminar flame burner and equipped with hollow-cathode emission lamps for the different metals sought. Metals sought were based on the stainless steel alloy, content of the catholyte, the atomic absorption spectrometry was used. Operating at 2.8 V. (n) Measured point.

\[
v_i = -L \frac{di}{dt}
\]

where $L$ is the wire inductance. For a 0.3 m long No. 4 AWG copper wire, the inductance is in the range of microhenry; however, the time rate of change of the current is about 2 $\times$ 10$^4$ A/s which caused the high potential drop.
The examination of Fig. 8 also reveals the interesting shape of the source potential waveform. Although the function generator produced a clean square wave, the resulting source potential waveform was far from being a clean one. For example, in Fig. 8 the source potential waveform has a step and a ringing at its trailing side instead of turning off at the 20th μs from pulse initiation. The shape of the source potential waveform during the off-time period of the pulse is the result of the induced potential in the No. 4 AWG wires and the cell’s maintained potential of 2.3 V. The induced potential in the No. 4 AWG wires connecting the cell to the power amplifier is caused by the discharge of current which is generated by the collapse of magnetic flux around these wires.

Using Eq. 1, the average electrical power delivered to the circuit and electrolyzer was calculated. For the circuit, the source potential and current waveforms were used; for the electrolyzer, the cell potential and current waveforms were used to calculate the power consumption. Subtracting these two sets of calculations gives the line losses which ranged from 13 to 18% of the circuit power demand compared to 5.5% in the nonpulsed dc case. The results for the electrolyzer average power consumption are summarized in Fig. 9. From this figure, one can conclude that the nonpulsed dc requires the least electrical power. This is in agreement with Viswanathan et al.’s numerical results. Their work concluded that the maximum rate of electrolysis for the intermittent potential case and consequently for all non-dc cases cannot exceed that for nonpulsed dc conditions. The effects of the pulse frequency and the duty cycle on the electrical power consumption are noticeable. For example, in Fig. 9 the demand for electrical power increases with the decrease of duty cycle and pulse frequency. The increase in the circuit’s electrical power demands can be attributed to two factors. The first is the line losses due to its inductive reactance and diode losses while the second factor is the increase in the electrolyzer’s internal losses. At a 10% duty cycle (Fig. 9), the electrolyzer’s power demand for 10 Hz is slightly more than twice that of nonpulsed dc while for 25 kHz the power demand is only 27% higher.

The increase in the electrolyzer’s internal losses can be explained using Ibi et al.’s model of the two diffusion layers with one layer pulsating near the electrode and another stationary layer further out in the electrolyte. For two diffusion layers, the activation overpotential would be larger than that of the single-layer nonpulsed dc operation. As the pulses get shorter (smaller frequency and/or duty cycle), both layers would be depleted before the initiation of the next pulse which requires higher overpotential to reactivate. These internal losses can be seen by examining the measurements of the catholyte and anolyte tempera-

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**Fig. 5.** Performance characteristics of the ICI electrolyzer using 10 w/o sulfuric acid. (□) Measured point.

**Fig. 6.** Hydrogen yield vs. current density for 10 w/o sulfuric acid. (□) Measured point, (-----) Faraday’s law.

**Fig. 7.** Applied current polarity reversal for 100 Hz and 50% duty cycle. (—) Potential, (—.--) current.

**Fig. 8.** Experimental setup response for 50% duty cycle and 25 kHz pulse at 100 cm³ hydrogen yield; (---) source potential, (------) cell potential, (----) current, (—.--) +ve lead potential drop.

**Fig. 9.** Electrolyzer power demands at 100 cm³ hydrogen yield. (□) 10 Hz, (□) 500 Hz, (△) 1 kHz, (○) 5 kHz, (■) 10 kHz, (▲) 25 kHz, (■) 40 kHz.
tures. The electrolyte temperatures were measured for monitoring purposes so as to keep the temperature below the 45°C required to keep the setup intact. For the 1 kHz pulse at 10% duty cycle case the electrolyte temperature increases by nearly 7°C above that of nonpulsed dc operation, while it increased only by about 2°C for the 80% duty cycle run.

One of the phenomena recorded by Bockris et al. in 1952 was not duplicated by this effort, namely, the high but short-lived current spike. However, the second phenomenon, significant current continuing to flow for a short time, was observed only when the diode was placed in the circuit. Bockris explained the cause of this phenomenon as the discharge of the ions in the double layer facing the electrode in the absence of the externally applied electric field. However, Fig. 7 shows that once the pulse was turned off the cell was free to discharge and the current reversed its polarity, i.e., the cell acted as a capacitance. When the diode was placed in the circuit, it prevented the cell from discharging and only the current that flowed in the right direction was allowed. Therefore, the current flow during the off-period of the pulse is largely due to the discharge of the current being generated by the collapse of the magnetic flux around the leads connecting the electrolyzer to the power amplifier.

The results of the present study show that the two-to-one improvement in electrolyzer performance predicted by Ghoroghchian and Bockris, Tsang and Vassie, and Jasem and Tseung did not materialize for the range of parameters studied. In these works the prediction was based on calculated pulsed current to nonpulsed current ratio. In the present study, the measurement of the hydrogen generation rate allowed an accurate comparison between the pulsed and nonpulsed dc operations.

Conclusions
The results of this work show that for the range of parameters studied pulsed dc is not ideal for water electrolysis. Conclusions can be summarized as follows:
1. The use of pulsed dc in a water electrolysis system will be accompanied by a reversal of the current polarity during the pulse off-period. Precautions should be taken to prevent this corrosive process.
2. Using pulsed dc in water electrolysis for hydrogen generation in the frequency and duty cycle ranges examined in this effort will increase the electrolyzer’s electrical energy usage.
3. Large reactive losses, produced by the inductive reactance which is caused by the current high rate of change, are expected.
4. Significant internal losses in the electrolyzer are expected. As the duty cycle or the frequency decreases, the current density required to maintain a hydrogen generation rate will increase. This will require higher overpotentials. The internal losses then convert to heat and increase the electrolyzer and electrolyte temperatures.

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REFERENCES
5. S. M. Jasem and A. C. C. Tseung, This Journal, 126, 1355 (1979).