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Model for the Electrolysis of Water and its use for Optimization

Cover Page Footnote

We thank Dr. Douglas Stuart, from the chemistry department at UWG, for his help with chlorine gas.

MODEL FOR THE ELECTROLYSIS OF WATER AND ITS USE FOR OPTIMIZATION

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ABSTRACT

The goal of this research was to study the optimization of the electrolysis of water both theoretically and experimentally. For accuracy, 3 hr experiments were made with measurements recorded every 15 min. The results show that a better model than the classical one is needed for water electrolysis. A new model that fits experimental data better is proposed. The results of this new model not only predict hydrogen production in electrolysis of water better, but show a way to predict gas production of any liquid as well as what voltage to use to optimize it.

Keywords: Optimization, electrolysis, salt, ohmic behavior, non-ohmic behavior, hydrogen production, hydrogen extraction, salt effects on electrolysis, quantum model for electrolysis, chemistry of electrolysis, salt in electrolysis.

INTRODUCTION

Many useful gases can be extracted through electrolysis of liquids. If one were to extract hydrogen from water for propulsion of spacecraft or earthly vehicles, it would be better, if not downright necessary, to do it in the optimum way. Based on the density of water and the ideal gas law, it can be shown that a cubic meter of water holds about 1360 times more hydrogen than is contained in the same volume of pure hydrogen gas at standard temperature and pressure (STP), even though the volume of hydrogen depends on temperature and pressure.

Electrolysis is a fairly well understood phenomenon for which there are many studies detailing the basics and some of the most complex details (Zoulias et al. 2014). Electrolysis has been tried to be optimized as part of a larger process (Saur and Ramson 2011). Whole systems of both hydrolysis cells and solar cells have been analyzed also (Ajayi et al. 2010). The search for a way to optimize the process has gone so far as to look for ways to optimize it in rotating magnetic fields (Bograchev and Davadov 2010). With our research here we looked purely at electrolysis in its most elemental form in order to study its optimization potential for a wide range of applications.

MATERIALS AND METHODS

To carry out our experiments the international Hoffman electrolysis apparatus was used as shown in Figure 1. The electrical power was supplied through a regulated power supply and the current was measured with an ammeter. The temperature was recorded using a thermometer constantly in contact with the water as shown in Figure 1. The experiments lasted a total of 3 hr each for accuracy of measurement of hydrogen and oxygen production. Measurements were taken every 15 min with the same voltage. The voltages were changed in intervals of 0.5 V. We used 100 mL of distilled water, obtained from the biology department at UWG, with 0.1 g of salt for conduction purposes. No additional catalyzer was used.

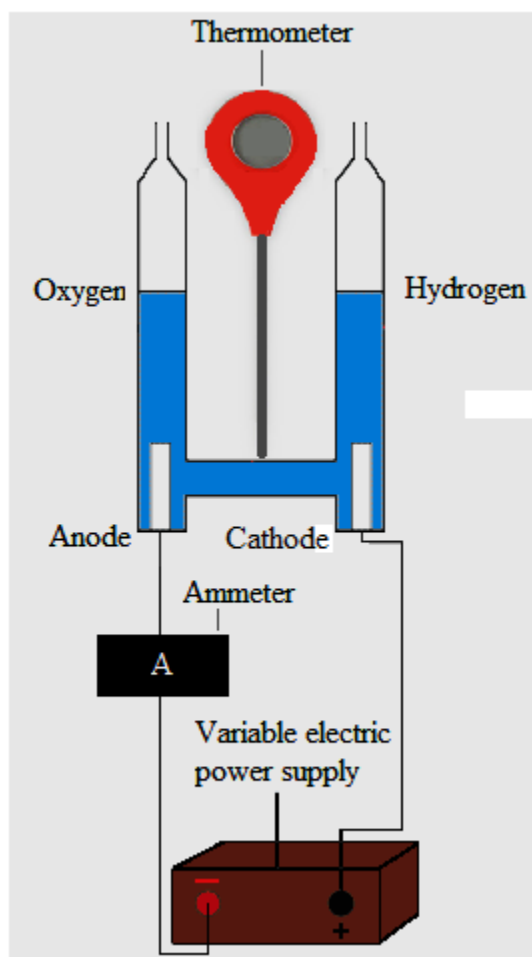


Figure 1. Laboratory setup.

CLASSICAL THEORY

According to the ideal gas law

$$V = \frac{nRT}{P}, \quad (1)$$

V is the volume, T is the temperature in Kelvin, P is the pressure, and n is the number of moles, and $R = 8.31445 \frac{J}{mol K}$ is the ideal gas constant.

For constant pressure and almost constant temperature, T, the above expression means that volume, V, is directly proportional to the number of moles liberated, n, but note that $n = \frac{N}{N_a}$, where N is the number of molecules and N_a is Avogadro's number. Both N and n are proportional to the number of bonds broken during electrolysis.

The first step in optimizing electrolysis is to model it using available equations. We are, with our power supply, providing power, P, to the water-electrolyte compound,

$$P_e = Iv, \quad (2)$$

where I is the current and v is the voltage.

Since P_e represents the amount of electrical energy supplied per second, we can use it to calculate the number of bonds that could be broken per second,

$$E_b \frac{n_b}{t} = Iv + \text{net energy losses}, \quad (3)$$

where E_b is the energy per bond, n_b is the number of bonds broken, and t is the time over which the electrical power is on.

Because it takes 926 kJ/mol to break two hydrogen-oxygen bonds but only 146 kJ/mol are gotten back from the oxygen-oxygen bond forming and 436 kJ/mol are gotten back from the hydrogen-hydrogen bond forming, there is a net energy loss in the system. At this point, experimentation is needed in order to continue with the optimization of electrolysis. Knowing the relationship between current and voltage for electrolysis will allow us to study equation (3) further below. For now it suffices to point out that in a classical model $v = Ir$ where r is the resistance, which would imply an ohmic behavior.

EXPERIMENTAL RESULTS AND ANALYSIS

Our experimental results regarding voltage and current are summarized in Table I. The voltage was increased at regular increments. Based on the classical theory, we expected water to have an ohmic behavior.

Figure 2 shows the graph of these results both with an ohmic fit and with a non-ohmic fit. The fits were made using the least squares algorithm. The figure shows that the ohmic fit does not accurately reflect the behavior of the data, as shown by its low goodness-of-fit R^2 value, shown in the figure. However, a power fit shows a better agreement with the experimental data. Based on a and b, coefficients of the power fit of figure 2, it is apparent that the current is proportional to the square of voltage and not to voltage itself.

According to our experimental data, therefore, we find that the relationship between current and voltage is better expressed as

$$I = kV^2, \quad (4)$$

$P = I^{3/2}/\sqrt{k}$. where k is a constant. This means that if we substitute V from equation (4) into equation (2), we get

$$P = I^{3/2}/\sqrt{k}. \quad (5)$$

Table I. Typical experimental results of voltage and current

<u>Current (mA)</u>	<u>Voltage (V)</u>	<u>Current (mA)</u>	<u>Voltage (V)</u>
0.32	4.0	4.18	14.0
0.38	4.5	4.26	14.5
0.58	5.0	5.10	15.0
0.70	5.5	5.37	15.5
0.90	6.0	5.31	16.0
1.03	6.5	6.41	16.5
1.19	7.0	6.32	17.0
1.35	7.5	6.29	17.5
1.52	8.0	6.73	18.0
1.84	8.5	7.68	18.5
2.01	9.0	7.22	19.0
2.05	9.5	8.18	19.5
2.23	10.0	8.80	20.0
2.41	10.5	8.93	20.5
3.03	11.0	9.95	21.0
3.05	11.5	9.06	21.5
2.95	12.0	9.91	22.0
3.32	12.5	11.38	22.5
3.58	13.0	13.98	23.0
4.40	13.5	15.23	23.5

However, if we combine equation (5) with equation (3), we arrive at the conclusion that the number of bonds broken per second is proportional to $I^{3/2}$. Combining this with equation (1), the ideal gas law, and noticing that pressure and liquid temperature are nearly constant in our experiment, having a maximum change of 0.3 °C, we find that the volume of hydrogen and oxygen produced should both be proportional to $I^{3/2}$. Figure 3, shows the experimental relationship between current and volume of hydrogen gas produced in our experimental results of Table II.

Because the volume of gas is rather proportional to the current it is clear, therefore, that a better model than the classical model is needed for gas production in electrolysis. Thus, the new model is based on the premise that each electron will break a bond. This model is based on the electron number instead of the energy. It can be thought of as a transportation model instead of a continuous model. Using this model we can calculate the theoretical hydrogen gas molecule production through electrolysis,

$$N = \text{number of electron pairs} = \frac{Q}{2e} = \frac{It}{2e}, \quad (6)$$

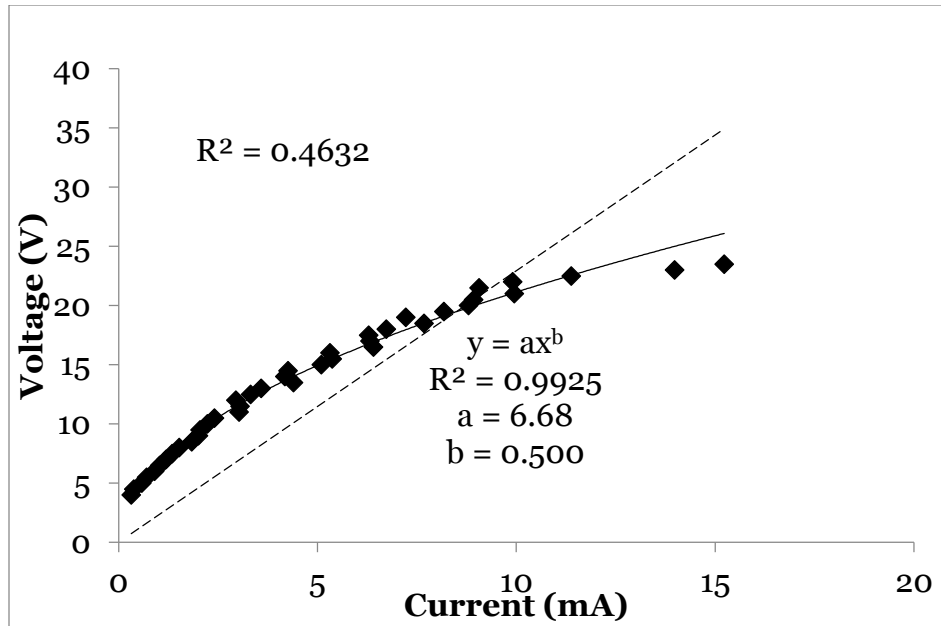


Figure 2. Relationship of voltage and current in the process of electrolysis for the experimental data of Table I. The ohmic fit is the dashed line. The non-ohmic power fit (solid line) shows a better R^2 value.

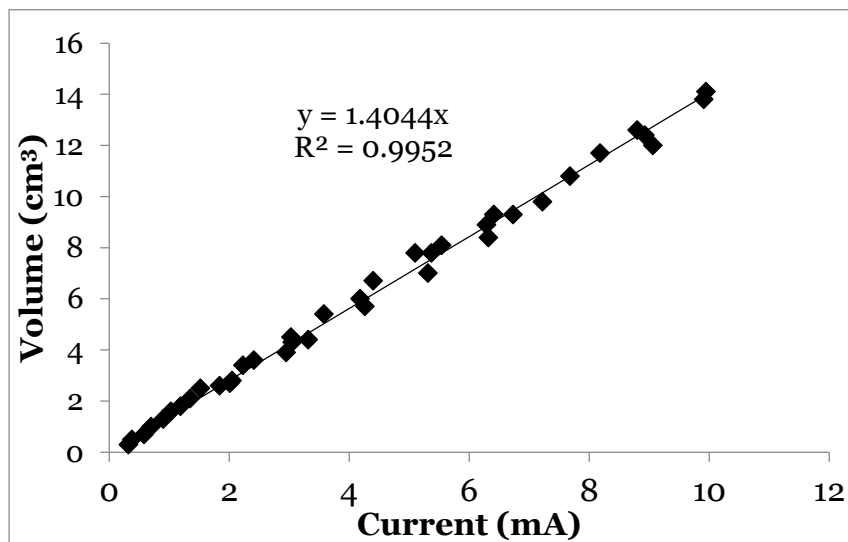


Figure 3. Relationship of current and hydrogen produced in electrolysis, as obtained in our experiment (see Table II).

Table II. Typical experimental results of average current, voltage, and H_2 volume.

<u>Average I (mA)</u>	<u>Voltage (V)</u>	<u>H₂ volume (cm³)</u>	<u>Average I (mA)</u>	<u>Voltage (V)</u>	<u>H₂ volume (cm³)</u>
0.32	4.0	0.3	4.4	13.5	6.7
0.38	4.5	0.5	4.18	14.0	6.0
0.58	5.0	0.7	4.26	14.5	5.7
0.70	5.5	1.0	5.10	15.0	7.8
0.90	6.0	1.3	5.37	15.5	7.8
1.03	6.5	1.6	5.31	16.0	7.0
1.19	7.0	1.8	6.41	16.5	9.3
1.35	7.5	2.1	6.32	17.0	8.4
1.52	8.0	2.5	6.29	17.5	8.9
1.84	8.5	2.6	5.54	18.0	8.1
2.01	9.0	2.7	6.73	18.0	9.3
2.05	9.5	2.8	7.68	18.5	10.8
2.23	10.0	3.4	7.22	19.0	9.8
2.41	10.5	3.6	8.18	19.5	11.7
3.03	11.0	4.5	8.8	20.0	12.6
3.05	11.5	4.3	8.93	20.5	12.4
2.95	12.0	3.9	9.95	21.0	14.1
3.32	12.5	4.4	9.06	21.5	12.0
3.58	13.0	5.4	9.91	22.0	13.8

where Q is the total charge and e is the electronic charge. Writing equation (1) as

$$PV = NRT/N_a, \quad (7)$$

and combining equation (7) with equation (6) and solving for the volume of hydrogen $PV = NRT/N_a$ produced, we arrive to the following expression for the theoretical volume of hydrogen production,

$$V_{H_2} = \frac{ItRT}{PN_a2e}. \quad (8)$$

Please note that everything else being equal, a higher temperature means a higher volume production. Based on this new theoretical model for hydrogen production and the experimental results, the efficiency of electrolysis in creating hydrogen gas can be calculated by taking the ratio of the theoretical volume to that obtained in our experiment of Table II.

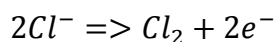
Thus, Table III contains the experimental average efficiency of hydrogen production over the 3 hr interval for each one of the voltages. This is plotted in figure 4. The data starts rather low, then it peaks and it slowly goes down with a lot of noise in it. The noise in the data has been found to correspond to temperature differences in the lab,

Table III. Calculated efficiency (ratio of equation (8) to experimental H_2 volume of table II) of the electrolysis process at the different voltages that the experiment was run at.

<u>Voltage (V)</u>	<u>Efficiency</u> <u>H_2</u>	<u>Voltage (V)</u>	<u>Efficiency</u> <u>H_2</u>
4.0	0.818	15.5	0.688
4.5	1.634	16.0	0.791
5.0	1.237	16.5	0.867
5.5	1.211	17.0	0.868
6.0	1.007	17.5	0.812
6.5	1.024	18.0	0.858
7.0	1.167	18.5	0.940
7.5	1.104	19.0	0.859
8.0	1.122	19.5	0.949
8.5	1.015	20.0	1.078
9.0	1.011	20.5	0.847
9.5	0.955	21.0	0.830
10.0	1.027	21.5	0.774
10.5	1.063	22.0	0.847
11.0	1.093	22.5	0.896
11.5	0.936	23.0	0.540
12.0	1.022	23.5	0.863
12.5	0.864	24.0	0.582
13.0	1.091	24.5	0.667
13.5	0.919	25.0	0.635
14.0	0.936	25.5	0.605
14.5	0.865	26.0	0.732
15.0	0.984	30.0	0.509

showing that the higher the temperature, the higher the efficiency, everything else being equal. The polynomial fit, shown with a solid line, shows a general downwards behavior, with a limit of efficiency tending to zero as the voltage tends to infinity.

It is also surprising that the efficiency goes above 1 in certain cases, which is not possible. Careful analysis of those results was made and the discrepancy was attributed to chemical reactions caused by the presence of salt (NaCl) in our solution as shown below. Ions in the salt dissociate; two Cl ions can join, producing chlorine gas and releasing two electrons in the process.



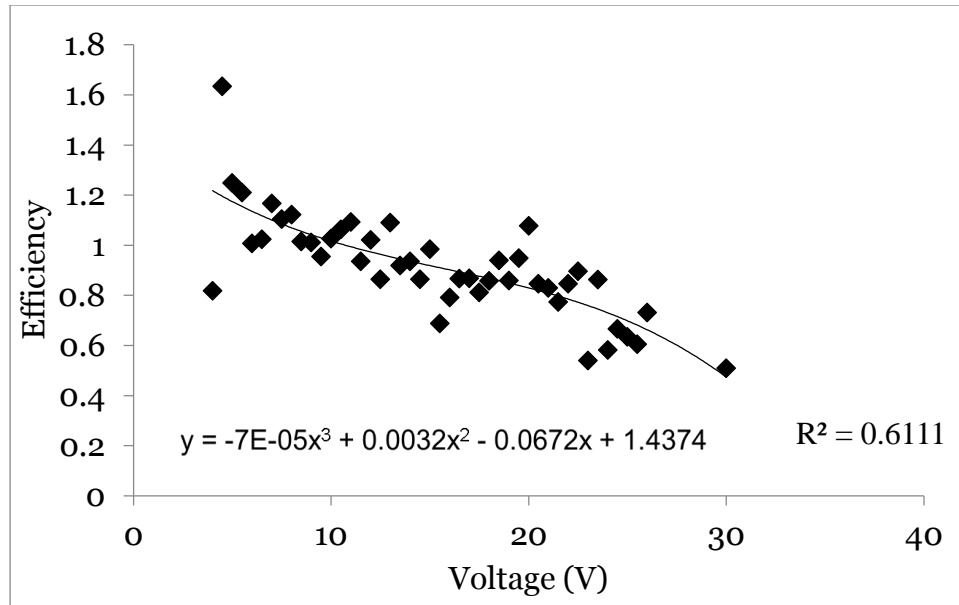
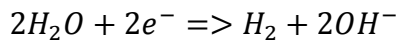
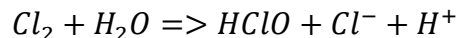


Figure 4. Average efficiency of hydrogen production during the 3 hr experiment interval using data from Table III. The solid line is a polynomial fit to guide the eye.

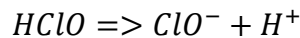
The released electrons react with two molecules of water, releasing a molecule of hydrogen gas.



Those two reactions have an unfortunate result which is the production of chlorine gas, which is known to be poisonous. However, after careful observation of the reaction no chlorine gas is detected and it is determined that any chlorine generated undergoes immediate hydrolysis to



Furthermore, HClO further breaks down into the components.



To verify the results, the same experiments were run with baking soda instead of salt. The amounts used were 0.1 g and 1 g in a 100 ml solution. Baking soda was found not to have the same effect as salt and the efficiency did not exceed unity because no reaction with chloride ions happened. The average efficiency shows the same behavior as in figure 4 but with lower values.

SUMMARY OF THE FINDINGS

The purpose of this research was to optimize electrolysis, and we collected enough data in order to develop our model. From equation (3) we know that, assuming maximum efficiency with no wasted energy,

$$E_b n_b = P * t \quad (9)$$

Combining equation (9) with equation (2) we find

$$It_{\text{optimal}} = E_b n_b \quad (10)$$

Thus according to this model, the optimum in electrolysis is to have each electron break one bond if it has enough energy to do so. In the case of water, each electron breaks one O-H bond, which can be expressed as

$$n_b = \frac{It}{e}, \quad (11)$$

for the number of broken O-H bonds.

Combining equations (10) and (11) and solving we get that, to optimize the electrolysis of any substance, we need an optimal voltage

$$v_{\text{optimal}} = \frac{E_b}{e}, \quad (12)$$

to break bonds and start the electrolysis process.

For water, that turns out to be 4.767 V (McMurry and Fay 2010). Our previous efficiency graph, Figure 4, shows the highest recorded value to be around 5 V; thus, there is preliminary agreement. However, when running the experiment at the exact optimum, the efficiency turned out to be different. It was found that a more appropriate equation is

$$V_{\text{optimal}} = C \frac{E_b}{e} \quad (13)$$

where the constant $C = 1.05$ is an empirically determined correction factor. Thus, to maximize the electrolysis of any liquid, it is important to run it at the optimum voltage. However, the current can be any value, and it will remain optimum. To adjust the current, the concentration of electrolyte could be increased or decreased and, in a complex enough machine that uses this process without the Hoffman electrolysis apparatus, the wires can be made to be closer or farther apart to regulate the current while keeping voltage constant.

CONCLUSIONS

This research shows that water does not behave according to Ohm's law and that the classical model needs improvement.

A quantum model in which each electron breaks one and only one bond as long as it has enough energy has been proposed. Based on this new model the voltage of peak efficiency is found to work better. The equation for the optimal voltage is significant because it can be used with any liquid and at any desired current.

Also, this research shows that certain electrolytes, like salt, can act as fuel in electrolytic processes which can be used for vehicles.

Moreover, because production increases as temperature increases, as reflected in the experimental data and equation (8), this process can be useful for hydrogen extraction on board vehicles because it is efficient and requires less space than carrying hydrogen by itself at STP.

Finally, because of its higher than unity efficiency when choosing the correct electrolyte (in this case salt, NaCl), this process could have many practical applications, like the use of electrolytes and water as fuel. However, to validate the model, experiments with electrolytes that do not affect the result, like the ones we performed with baking soda (NaHCO_3), are necessary.

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We thank Dr. Douglas Stuart, from the chemistry department at UWG, for his help with chlorine gas.

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