

Active Learning of Electrochemical Engineering Principles Using a Solar Panel/Water Electrolyzer/Fuel Cell System

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Equipment

The experimental system, pictured in Fig. 1, is a commercially available unit (Junior Basic; H-Tec; <http://www.h-tec.com>) comprised of a 2 V/ 350 mA solar panel, a 1.0 W proton exchange membrane (PEM) water electrolyzer, 20 cm³ hydrogen and oxygen storage reservoirs, a 500 mW PEM fuel cell and a 10 mW electric load (fan), all mounted on a base plate. Additional equipment needed to run a full range of experiments are a spotlight (a desk lamp is adequate), a variable dc power supply (5 V, 5 A), a handheld multimeter, connector cables, and a variable resistor load box. The Junior Basic set allows students to observe how energy from photons

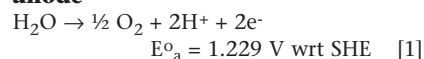
(solar/lamp energy) is converted to electricity, which in turn is used to electrolyze water to produce hydrogen and oxygen. The hydrogen and oxygen gases generated by water electrolysis are stored in cylinders and are fed to the fuel cell, which powers the fan. The cost of the Junior Basic Set is \$250. and it may be purchased in the U.S. at www.fuelcellstore.com. Accessory equipment can be borrowed from most electrical engineering/physics departments or purchased for ~\$200 to 300 per set. More sophisticated experiments are possible if a potentiostat is available or can be purchased (\$1,000-\$10,000).

Background Information and Equations

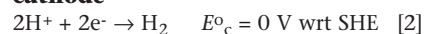
The following information can be presented to students either before running the experiments or, in an inductive approach, can be discussed after the experiments have been run.

Thermodynamics.—Electrochemical reactions are classified as either electrolytic or galvanic processes.⁹ An electrolytic process is a non-spontaneous process where chemical change is achieved by passing electrical energy through a device, *i.e.*, energy must be provided for the electrochemical reaction to proceed. An example of such a process is water electrolysis. In water electrolysis, the anode, cathode, and overall reactions are

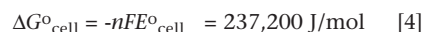
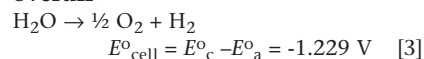
anode



cathode



overall



The reaction is not thermodynamically favored as $\Delta G^\circ_{\text{cell}}$ is positive.

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As resources of fossil fuels are rapidly consumed at a rate that far exceeds new discoveries, it is evident that a transition to a renewable and sustainable energy economy is essential for continued progress. The specter of global climate change caused by excessive release of greenhouse gases like carbon dioxide requires that any new energy economy be CO₂ neutral in addition to being renewable and sustainable. Such an economy is no more than an ideal as of today. Transforming this ideal into reality will require years of dedicated research and development and will likely involve the next generation(s) of scientists and engineers. It is therefore imperative that these generations are attracted at an early stage toward careers in science and engineering, especially energy related fields. To this end, the primary objective of this article is to provide instructors with active learning modules that can be disseminated to students throughout the undergraduate curriculum in relevant disciplines such as chemistry and chemical engineering. The modules have been designed to be instructor friendly, *i.e.*, they are simple and the associated experiments (in most cases) can be performed during a normal lecture period. The equipment used in these experiments is relatively inexpensive compared to pilot-scale equipment of similar nature, thereby allowing the purchase of multiple setups for use in a single class. An excellent instruction manual¹ is provided by the manufacturers of the solar panel / electrolyzer / fuel cell system and many experiments described in this paper are adaptations of experiments described in the manual.

The effectiveness of these modules can be enhanced by preceding their use with discussions/assignments related to renewable and sustainable energy economies. Suggested topics for discussion include

1. Are we too reliant on fossil fuels?
2. What is the environmental impact of fossil fuels (vs. other energy sources)?
3. Are oil and gas reserves in danger of running dry within the foreseeable future?
4. What are some alternative sources of energy and their advantages and disadvantages?
5. Is energy independence crucial to our economy and our country's security?
6. Why use hydrogen? Are there other fuels?
7. What are the environmental and economic advantages of hydrogen?
8. How can we produce hydrogen? Is hydrogen safe?
9. How can hydrogen be stored?
10. What is global warming? How do greenhouse gases contribute to global warming?
11. What are renewable and sustainable energy economies?

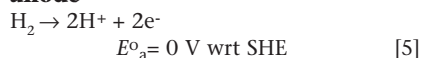
The above list is by no means exhaustive. Information regarding these topics can be found in Ref. 1-8. It is anticipated that the use of these modules (and associated discussions) will stimulate interest in the area of fuel cells and associated technologies. The experiments accompanying these modules provide a concrete demonstration of the possibility of providing non-polluting, renewable, and sustainable energy.

Fenton, et. al.
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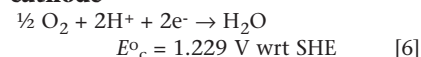
In these equations, 1.229 and 0 represent the potential (in volts) of the anode and cathode reactions with respect to the standard hydrogen electrode (SHE), E°_{cell} is the standard voltage of the overall reaction, $\Delta G^{\circ}_{\text{cell}}$ is the change in Gibbs free energy where n is the number of electrons participating in the reaction (units of equivalents/mole), and F is Faraday's constant (96,485 C/equiv). The superscript $^{\circ}$ indicates standard conditions: 25°C and unit activity for the species. A positive change in Gibbs free energy means the reaction is not thermodynamically favored to proceed in the direction indicated, *i.e.*, toward the products. The reader is directed to Ref. 9 for further information on electrochemical engineering principles and conventions.

A galvanic process is a spontaneous process where electrical energy is produced by chemical change. Batteries and fuel cells are examples of galvanic processes. The electrochemical reactions in a hydrogen/oxygen fuel cell are

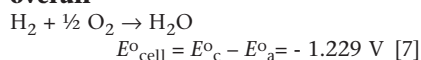
anode



cathode



overall



$$\Delta G^{\circ}_{\text{cell}} = -nFE^{\circ}_{\text{cell}} = -237,200 \text{ J/mol.}$$

The reaction is thermodynamically favored as $\Delta G^{\circ}_{\text{cell}}$ is positive.

Clearly, the role of free energy in determining spontaneity can be demonstrated along with its physical significance, *i.e.*, one must impart energy to electrolyze water (consuming energy) vs. the fuel cell which produces energy. Although a reaction may be thermodynamically favored, it may not proceed at a significant rate because of kinetic, ohmic, and transport limitations.

The maximum available voltage from a galvanic process, or the minimum decomposition voltage in electrolysis, involves thermodynamic evaluation of energy differences between the initial state of the reactants and the final state of the products (reversible voltage or E). Maximum available or minimum decomposition voltage is useful for calculating efficiencies and for determining upper (or lower) limits of performance. Thermodynamic equations relate reversible voltage to state variables. Sample calculations taken from Ref. 10 (see Table I.) show how voltage varies with tem-

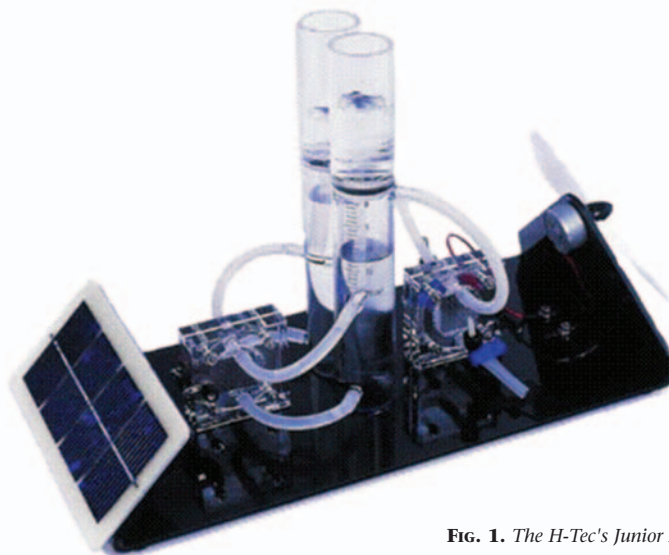


FIG. 1. The H-Tec's Junior Basic System.

Table I. Sample Calculations – Reversible voltage at varying temperatures for the H₂/O₂ fuel cell.

For $P = 1 \text{ atm}$, 25°C , 1 mol of H ₂ reacting	For $P = 1 \text{ atm}$, 80°C , 1 mol of H ₂ reacting
$\Delta G = \Delta H - T\Delta S$ $= -285,840 \text{ J/mol} - (298 \text{ K})(-163.2 \text{ J/mol K})$ $= -237,210 \text{ J/mol}$ $\Delta E = -\Delta G / nF$ $\Delta E = -\frac{(-237,210 \text{ J/mol})}{2 \text{ equiv/mol} \times 96,485 \text{ C/equiv}}$ $= 1.23 \text{ J/C} = 1.23 \text{ V}$	<p>The values of ΔH and ΔS change only slightly compared to T.</p> <p>ΔG is approximated as</p> $\Delta G = -285,840 \text{ J/mol} - (353 \text{ K})(-163.2 \text{ J/mol K})$ $= -228,230 \text{ J/mol}$ $\Delta E = -\frac{(-228,230 \text{ J/mol})}{2 \text{ equiv/mol} \times 96,485 \text{ C/equiv}}$ $= 1.18 \text{ V}$

perature for the H₂/O₂ fuel cell reaction at unit activity for the gaseous reactants and liquid water product.

The Nernst equation can be used to calculate reversible voltage at nonstandard concentrations and a given temperature. Equation 8 is the Nernst equation specifically written for the H₂/O₂ reactions given in Eq. 5, 6, and 7.

$$E = E^{\circ} + \left(\frac{RT}{nF}\right) \ln \frac{[P_{\text{H}_2}][P_{\text{O}_2}]^{1/2}}{[P_{\text{H}_2\text{O}}]} \quad [8]$$

where R = gas constant (8.314 J/mol K), E° = reversible voltage at standard concentrations and temperature T , E = reversible voltage at non-standard concentrations and temperature T , and

P_{H_2} , P_{O_2} , $P_{\text{H}_2\text{O}}$ = partial pressures of H₂, O₂ and H₂O (atm), respectively, which approximates the activities of H₂(g), O₂(g), and H₂O(l).

Stoichiometry.—There is a direct relationship between the charge passed (current consumed or produced) and the amount of product formed or reactant consumed in electrochemical reactions. The relationship is described by Faraday's law

$$I = \frac{nmF}{SMt} \text{ (A)} \text{ or rearranged } \frac{m}{Mt} = \frac{I}{nF} \text{ (mol/time)} \quad [9]$$

where I (A) is the current, m (g) is the mass of product formed (or reactant consumed), n and F are defined above,

s is the stoichiometric coefficient of either the product or reactant species, M (g/mol) is the atomic or molecular mass of the product (or reactant) species, and t (s) is the time elapsed. Equation 9 is valid for a constant current process. In the electrolysis of water, the current consumed by the electrolyzer is directly proportional to the volume of H_2 and O_2 generated (observable and quantifiable using the Junior Basic kit). Similarly, in the H_2/O_2 fuel cell, the current generated is directly related to the hydrogen and oxygen consumed. An example of fuel cell feed flow rate calculation involving Faraday's law, the Ideal Gas law, and the concept of fuel utilization is shown in Table II. Note that fuel cells are typically run under conditions of excess fuel (fractional utilization).

Current-Voltage Characteristics, Power, and Efficiency.—The performance of devices such as fuel cells and electrolyzers is typically demonstrated by plotting the current or current density (current per active area of the unit) against the cell voltage. This performance curve along with thermodynamic information allows calculation of efficiency. In fuel cells, the maximum attainable cell voltage (measured at equilibrium, *i.e.*, infinite resistance-no current flowing) is a function of the change in Gibbs free energy for the reactions occurring in a fuel cell. When a finite resistance or load is applied to the cell, the cell moves away from equilibrium and a current flows. There is a trade-off between current (I) and voltage (V) at non-equilibrium conditions. By varying the load resistance applied to the cell and recording the corresponding voltage and current, one can generate a characteristic V - I curve (Fig. 2). The current density (current/active area) vs. voltage curve (polarization curve) for a typical fuel cell will reflect losses due to kinetic, ohmic, and mass transfer resistances. Performance losses due to these limitations have been described in detail in Ref. 11.

The power generated by the fuel cell at any given point on the polarization curve can be determined by multiplying the current and voltage at that point. The efficiency of the fuel cell can be defined several ways.⁹ The current efficiency, ϵ_i , is defined as

$$\epsilon_i = \frac{\text{Current produced by the fuel cell}}{\text{Theoretical amount of current that should be produced (Faraday's law)}} \quad [10]$$

The voltage efficiency, ϵ_v , is defined as

$$\epsilon_v = \frac{\text{Actual cell voltage}}{\text{Reversible cell voltage}} = \frac{V}{E} \quad [11]$$

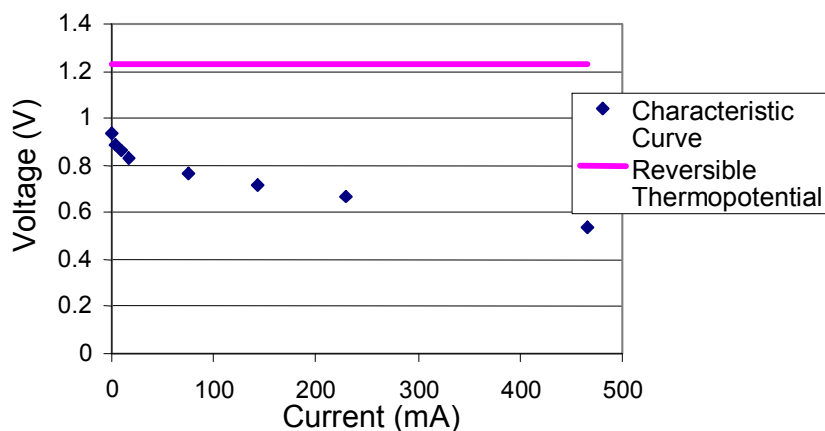


Fig. 2. Fuel cell performance curve.

Table II. Sample Calculations – Fuel cell feed flow rate for 45% H_2 utilization at 1A.¹¹

<p>Faraday's law: or $P = \frac{m}{Mt} = \frac{I}{nF}$ mol/time</p> <p>Hydrogen consumption in fuel cell = $I/(2F)$ mol/time</p> <p>To produce a current of 1A, H_2 consumption is</p> <p>$= 1/(2F) = 1/(2 \times 96485) = 5.18 \times 10^{-6}$ mol/s</p> <p>$= 3.11 \times 10^{-4}$ mol/min</p> <p>According to the gas law $PV = NRT$</p> <p>At 353 K; 1 atm $V/N = 0.082 \times (353)/1$</p> <p>$= 29$ L/mol</p>	<p>So H_2 consumption is $V_{H_2} = 3.11 \times 10^{-4} \times 29 = 9.0$ mL/min</p> <p>O_2 consumption is $V_{O_2} = 4.5$ mL/min</p> <p>Corresponding $V_{air} = 4.5/0.21 = 21.4$ mL/min</p> <p>For desired 45% H_2 utilization at 1 A current: H_2 feed flow rate is $V_{H_2} = 9.0/0.45 = 20$ mL/min at 1 A</p>
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Overall energy efficiency, ϵ^T , is defined as the product of the current and voltage efficiencies

$$\epsilon^T = \epsilon_i \epsilon_v \quad [12]$$

Typical fuel cell overall efficiencies are about 40-50%. Current and voltage efficiencies for the electrolyzer are inverted versions of Eq. 10 and 11, respectively.

Kinetics.—The rate at which an electrochemical reaction proceeds is proportional to the current input to or current production from the device. Faraday's law can be rewritten to show this relationship. For example, for the H_2/O_2 fuel cell the rate of reaction can be represented as

$$\frac{I}{2F} = \frac{d(\text{moles } H_2O)}{dt} = \frac{-d(\text{moles } H_2)}{dt} = \frac{-2d(\text{moles } O_2)}{dt} \quad [13]$$

Thus, kinetic rates can be calculated directly from current measurements in electrochemical devices. The kinetic

behavior of the fuel cell can be analyzed using the low current density portion of the characteristic V - I curve. At these conditions, reactants are plentiful (no mass transfer limitations) and the current density is so small that ohmic losses (current \times resistance) are negligible. Deviations from reversible voltage in this region are due primarily to kinetic losses. The Tafel equation describes the current density-voltage polarization curve in the kinetically controlled region

$$\eta^{\text{act}} = B \log |i| - A \quad [14]$$

where η^{act} is the voltage loss (mV) due to slow kinetics, i is the current density (mA/cm²), and constants A and B are kinetic parameters (B is called the Tafel slope). The theoretical Tafel slope is equal to $2.303RT/\alpha F$ where R is the ideal gas constant, T is absolute temperature, F is Faraday's constant, and α is a lumped kinetic parameter (with values between 0 and 1; typically assumed to be 0.5 for the oxygen reduction reaction occurring on the cathode).⁹ According

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Fenton, et. al.

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to this theory, the Tafel slope should be independent of reactant concentration and can be found experimentally by plotting $\eta^{\text{act}}(E - V)$ vs. $\log i$ and measuring the slope of the line in the kinetically controlled portion of the plot (at low values of $\log i$).

Active Learning Modules

The solar panel / water electrolyzer / fuel cell system was used as part of a chemical engineering undergraduate elective course, Fuel Cell Engineering, in spring 2003 and fall 2004 (taught by J.M.F. at the University of Connecticut). The modules described below have evolved from that course.

Stoichiometric module

Demonstration of law of proportions.—To perform these experiments one needs an external power supply or battery, a Junior Basic set, and a stopwatch. Setup and procedures are detailed in the Junior Basic instruction manual.¹ The electrolysis experiment is started with water in both H₂ and O₂ storage tanks maintained at an identical level. An external power supply or battery is used to drive the electrolysis reaction at a known current for a fixed amount of time. The volume of gas in the two cylinders is measured after the electrolysis reaction is stopped. The twofold production of hydrogen (with respect to oxygen) is visually seen by the twofold volume of gas produced in the hydrogen cylinder. Sample H₂ and O₂ volume data obtained at different electrolyzer current inputs are presented in Table III. The ideal gas law was used to convert the gas volumes to moles.

Demonstration of Faraday's law.—The electrolysis experiment is performed as described above, with time and current passed carefully noted. The volume of hydrogen/oxygen generated can be estimated and used to determine the moles of hydrogen produced (Table III). This value can be compared to the theoretical number of moles expected for the given current passed and time of passage obtained via Faraday's law. These values can be used to determine the current efficiency of the electrolysis process (Table III). Typical current efficiencies for electrochemical devices are slightly less than 100%. The efficiencies exceeding 100% reported in Table III are attributed to errors in estimating gas volumes. Faraday's law can also be used in a similar manner with the fuel cell to calculate current efficiency. A scale-up problem can be introduced at this point, for example, students can be asked to predict the length of time the electrolyzer would have to be run if

50 mL of H₂ is to be generated. From a fuel cell viewpoint, the students can be asked to calculate the amount of hydrogen needed to run an automobile (typically a 50-70 kW fuel cell) for a specified amount of time, and the pressure in the storage tank (of fixed volume) that would be necessary to accommodate this amount of hydrogen.

Thermodynamics Module

Galvanic vs. electrolytic process.—The concept of spontaneity (with respect to the sign of the change in Gibbs free energy) can be readily demonstrated. Operation in electrolyzer mode (water electrolysis reaction) results in a positive ΔG . The non-spontaneity of this process is evident in that an external power source is necessary to commence the reaction even when the reactant (water) is available in plenty. While running in galvanic mode (fuel cell), the ΔG is an identical number but is negative. The spontaneity of the reaction is seen by the instantaneous movement of the propeller (motor) when the hydrogen and oxygen are allowed to enter the fuel cell. As an exercise, students can be asked to write a paragraph on the thermodynamic (and practical) feasibility of an electrolyzer-fuel cell system if electricity is to be obtained from the grid.

Variation of cell voltage with reactant concentration.—The theoretical open circuit voltage can be calculated for oxygen and air as oxidants (oxygen concentration changes by a factor of five) at any given temperature using calculated values of ΔG (see Table I) and the Nernst equation (Eq. 8). A lower theoretical value will be obtained when air is used in the calculations. This can be experimentally verified by measuring open circuit voltage when the fuel cell is contacted with oxygen (from electrolyzer) and air (from atmosphere), respectively.

To perform these experiments one needs a Junior Basic set and a multimeter. Both values will fall short of the theoretically predicted values. For example, the theoretical open circuit voltage using oxygen at 25°C should be 1.23 V (sample calculation 1). However, as seen in Fig. 3, the observed open circuit voltage is 0.924 V. This results in a calculated voltage efficiency of 75%. At this point a question can be posed to students about the observed discrepancy. A proposed explanation for the discrepancy can be found in Ref. 9.

Performance Characteristics and Efficiencies Module

Determination of performance characteristics.—The performance characteristics of the fuel cell may be obtained by connecting the fuel cell output to a variable resistor load, and changing the load resistance to obtain different current outputs. The voltage can be simultaneously measured across the fuel cell using a multimeter. Setup and procedures are detailed in the Junior Basic instruction manual.¹ A picture of the experimental setup is presented in Fig. 3. Performance curves can be obtained for different steady-state hydrogen and oxygen flow rates (controlled by maintaining desired electrolyzer current). Experiments can also be run using air as the oxidant rather than oxygen by disconnecting the oxygen line from the fuel cell and operating it in air breathing mode. The current (or current density, which is the current divided by the active area of the fuel cell) is plotted vs. cell voltage to yield a polarization curve (Fig. 2). The power characteristics may be obtained by multiplying each current by the corresponding voltage to yield power, and plotting against current. The curves obtained using different reactant flow rates can be compared. Similarly, electrolyzer performance characteristics can be obtained

Table III: Stoichiometric module — sample data.

Time (s)	O ₂ vol cm ³	H ₂ vol cm ³	O ₂ /H ₂ (mol ratio)	H ₂ produced from data (mol)	H ₂ produced Faraday's law (mol)	Calculated Current Efficiency
Current input to electrolyzer = 2.4 A						
30	5	11	0.45	0.000449	0.000373	120.44
60	9	18	0.50	0.000735	0.000746	98.54
Current input to electrolyzer = 0.5 A						
60	2.7	4	0.68	0.000163	0.00155	105.11
120	4.2	8	0.53	0.000327	0.000311	105.11
180	6.2	11.8	0.53	0.000482	0.000466	103.36
240	8	15.5	0.52	0.000633	0.000622	101.82
300	9.8	19.5	0.50	0.000797	0.000777	102.48

Average O₂/H₂ mol ratio = 0.53; Standard Deviation = 0.07

by measuring the voltage across the electrolyzer as it operates under different currents dialed in using the power supply.

Determination of operating efficiencies.—

The voltage efficiency of the fuel cell at a given current density is given by Eq. 11 as the ratio of the operating voltage to the theoretical voltage (vice versa for electrolyzer voltage efficiency). The current efficiency of the fuel cell at a given flow rate is the ratio of the current generated to the current that can be obtained if Faraday's law is followed (Eq. 10). For the electrolyzer, it is the amount of hydrogen produced to the amount that would be produced if Faraday's law is followed. The overall energy efficiencies of the fuel cell and electrolyzer may be obtained using Eq. 12, and the total system efficiency obtained by multiplying the two overall efficiencies.

Kinetics Module

*Estimating kinetic parameters.—*Kinetic parameters can be obtained from the performance characteristics in the low current density (high load resistance) region, where ohmic and mass transport effects do not overly convolute the data. The results can be analyzed using the Tafel equation. This is best done by plotting the data as a semi-log plot [($E - V$) vs. log (current density)]. The data should then lie on a straight line, the slope of which is equal to the Tafel slope. This is shown in Fig. 4. The Tafel slope in this case is calculated to be $2.303 \times 0.042 = 0.097$ V/decade = 97 mV/decade. Multiplication by 2.303 is to convert from natural log to log base 10. A theoretical Tafel slope ($RT/cnF = 60$ mV/decade at 298 K) is indicative of a kinetically controlled reaction, which is the ideal scenario. In this case, the calculated Tafel slope is almost 100 mV/decade – a significant deviation from the theoretical value. This deviation is attributed to ohmic and mass transport losses in the system.

Concluding Remarks

This article describes how a simple, readily available device can be used effectively to promote active learning in the classroom, raise awareness regarding future energy economies, and stimulate interest in fuel cell and related electrochemical engineering technologies among engineering students. Included is a brief description of the principles of stoichiometry, thermodynamics, kinetics, and performance/efficiencies associated with the solar panel / electrolyzer / fuel cell device, with emphasis on the electrolyzer and fuel cell components. Modules facilitating hands-on learning of these traditional principles are presented. These modules have been implemented by the authors at the undergraduate level with positive results, and should be useful in future science and engineering classes.

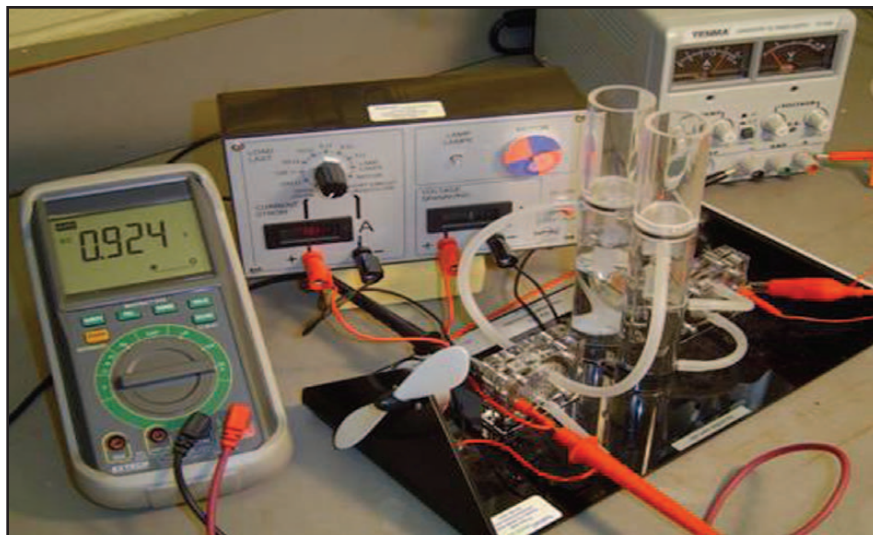


FIG. 3. Experimental setup to obtain fuel cell performance characteristics.

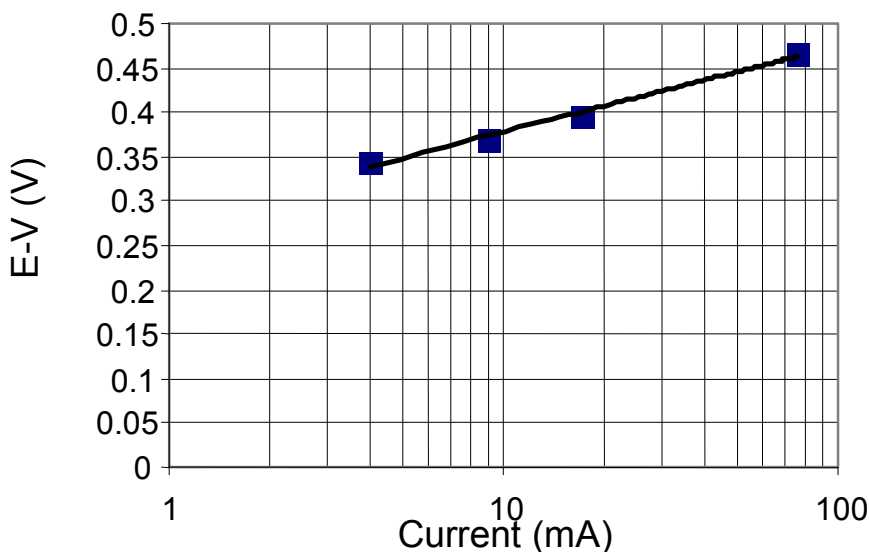


FIG. 4. Estimation of kinetic parameters.

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Fenton, et. al.

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