

Hydrogen Storage Experiments for an Undergraduate Laboratory Course—Clean Energy: Hydrogen/Fuel Cells

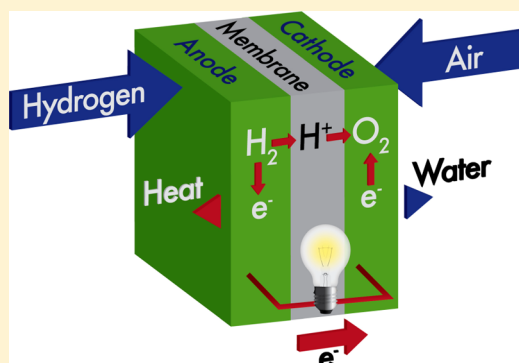
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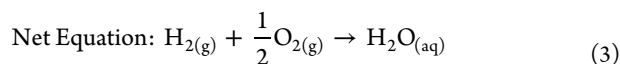
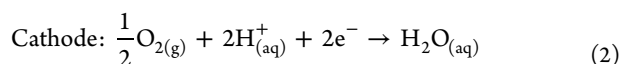
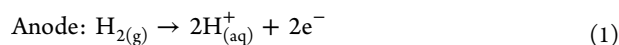
S Supporting Information

ABSTRACT: Global interest in both renewable energies and reduction in emission levels has placed increasing attention on hydrogen-based fuel cells that avoid harm to the environment by releasing only water as a byproduct. Therefore, there is a critical need for education and workforce development in clean energy technologies. A new undergraduate laboratory course for students has been developed, entitled, Clean Energy: Hydrogen/Fuel Cells. If hydrogen is to be used on a large-scale basis, the storage of hydrogen becomes a crucial issue for mobility and transport applications. Fuel cell technology would be practical if hydrogen could be stored in a safe, efficient, compact, and economic manner. The experiments reported here train students to measure the hydrogen storage capacity of aqueous hydrochloric acid solution and solid magnesium hydride by measuring the consumption of hydrogen with a hydrogen fuel cell and evaluating its performance. In addition, students also gain fundamental experience handling gases and using the gas law equations.

KEYWORDS: First-Year Undergraduate/General, Green Chemistry, Laboratory Instruction, Environmental Chemistry, Hands-On Learning/Manipulatives, Applications of Chemistry, Electrolytic/Galvanic Cells/Potentials



Meeting energy needs in a sustainable and environmentally responsible way is currently a major global challenge. Some strategies to address this problem are to involve very efficient uses of energy as well as renewable and sustainable (carbon-neutral) energy sources. A fuel cell converts chemical energy to electric energy with high efficiency. Often hydrogen is the energy storage medium in the fuel cell and oxygen the oxidizer, as shown in the abstract image and in eqs 1–3, and only the environmentally friendly water is released as the byproduct.^{1–3}



The most promising renewable energy to support the clean energy needs of the future is sunlight, which produces hydrogen by photoelectrolysis of water. Chemical education projects involving laboratory research experiments with secondary classrooms, undergraduate institutions, and outreach activities have been developed, which result in inexpensive, stable metal oxide semiconductors for use in water splitting by solar photoelectrolysis.⁴ In addition, creating educational materials related to hydrogen fuel cells is important for future workforce development. Since 2008, a course entitled “Clean Energy: Hydrogen/Fuel Cells” has been offered at least twice annually

in both lecture and online formats to students who have completed one undergraduate general chemistry course.^{2,5,6} The course concludes with student assembly and testing of the performance of a proton exchange membrane (PEM) fuel cell in the laboratory.⁷ An undergraduate “Clean Energy: Hydrogen/Fuel Cells Laboratory” course has also been developed and offered five times since 2011.⁸

If hydrogen is used on a large-scale basis, the storage of hydrogen becomes a crucial issue for mobility and transport applications. Fuel cell technology would be practical if hydrogen could be stored in a safe, efficient, compact, and economic manner.² Since many compounds contain hydrogen, the goals of these experiments are to measure the hydrogen storage capacity of: (1) aqueous hydrochloric acid solution via reaction with Zn metal and (2) solid magnesium hydride by hydrolysis in the presence of acetic acid using an ideal gas law apparatus for hydrogen yield measurement and consumption of hydrogen by a fuel cell. Metal hydrides are advantageous for storage of hydrogen in a solid compound because high volumes of hydrogen are contained in small masses of metal hydride.

These experiments illustrate fundamental principles for handling gases and important gas law equations, offering direct experience with a hydrogen fuel cell and evaluating its performance, and introducing the concept of hydrogen storage materials, which is a central issue in the development of hydrogen economy. The total time for the experiment is about

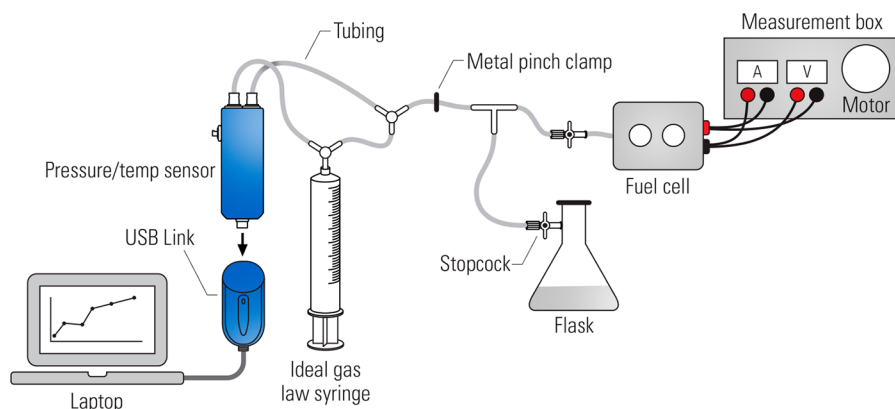


Figure 1. Apparatus for measuring the amount of produced hydrogen with fuel cell, motor, ideal gas law equipment, and laptop computer.

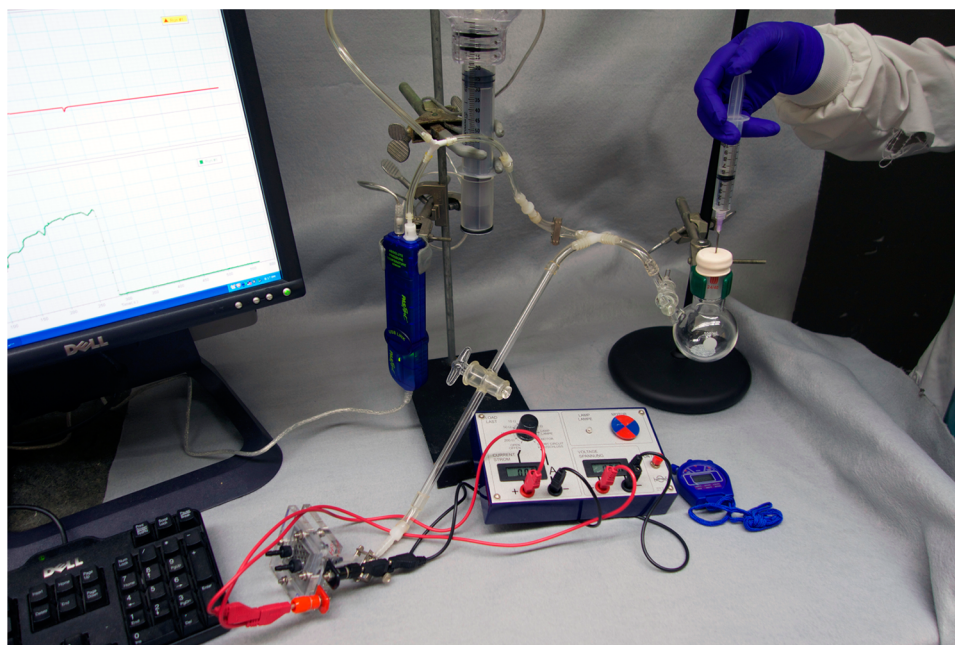


Figure 2. Experimental setup of equipment for determining hydrogen storage capacity of hydrogen-containing materials.

2 h including prelab discussion, equipment setup, and conducting the experiment.

Some previously published experiments, related to the subject of this paper, are (i) Photocatalytic Hydrogen Production by Direct Sunlight;⁹ (ii) Electrolysis of Water and the Hydrogen–Oxygen Fuel Cell;¹⁰ (iii) Photoassisted Fuel Cell To Remediate Simulated Wastewater;¹¹ (iv) PEM Fuel Cell Test Station and Laboratory Experiment;¹² and (v) Fuel Cells: An Ideal Chemical Engineering Undergraduate Experiment.¹³

■ EXPERIMENTAL PROCEDURES

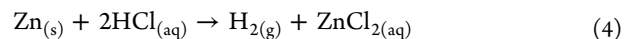
Experiment 1a: Hydrogen Storage Capacity of Hydrochloric Acid via Reaction with Zinc

Granular zinc metal (2 g) is placed in a 100 mL round-bottom flask with a glass stopcock side arm port (Kemtech America, Inc.). A plastic adapter is connected with plastic tubing from the stopcock on the round-bottom flask to the fuel cell (Fuel Cell Store, Dr. Fuel Cell Dismantable Fuel Cell Extension Kit), which has a measurement box (Dr. Fuel Cell Load Measurement Box) that reports voltage and current during movement

of a motor on the box. Another plastic three-way adapter is connected to a pressure/temperature sensor with tubing to both the fuel cell and an ideal gas syringe (PASPORT Ideal Gas Law Apparatus, TD-8596A)¹⁴ as shown in Figure 1.

To determine the hydrogen storage capacity of hydrochloric acid via reaction with zinc, the stopcock/pinch clamp connected to the ideal gas law apparatus is closed, and a septum stopper is attached to the 24/40 joint on the flask in order to add 8.0–10.0 mL of 3.0 M hydrochloric acid all at once using a syringe to produce gaseous hydrogen. Figure 2 shows the equipment setup in a vacuum hood.

Gaseous hydrogen is formed as a product of the single replacement in reaction 4.



The energy carrier, hydrogen, is then converted into electric energy by the fuel cell, and readings are taken of the current, voltage, and time when the motor is running.

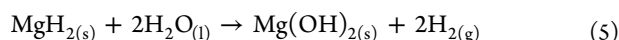
Table 1. Measurements for the Reaction of 2.0 g of Zn with 8.8 mL of 3.0 M HCl Solution

t (s)	I (amps)	V (volts)	W (watts)	H_2 (g(10^{-5})) ^a	H_2 (mol(10^{-5})) ^a
10	0.014	0.74	0.010	0.15	0.074
30	0.014	0.74	0.010	0.44	0.22
60	0.014	0.73	0.010	0.88	0.44
90	0.014	0.73	0.010	1.3	0.63
150	0.014	0.72	0.010	2.2	1.1
210	0.014	0.71	0.0099	3.1	1.5
270	0.014	0.71	0.0099	4.0	2.0
330	0.014	0.70	0.0099	4.8	2.4
390	0.014	0.70	0.0098	5.7	2.8
450	0.014	0.70	0.0098	6.6	3.3
510	0.014	0.70	0.0098	7.5	3.7
570	0.014	0.70	0.0098	8.3	4.1
630	0.014	0.70	0.0098	9.2	4.6

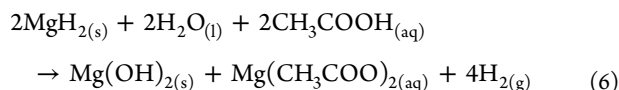
^aConsumption of hydrogen in grams and moles.

Experiment 1b: Hydrogen Storage Capacity of Magnesium Hydride

Hydrogen production during hydrolysis of MgH_2 in the presence of acetic acid is measured. As shown in reaction 5, gaseous H_2 is released when solid MgH_2 reacts with liquid H_2O .



However, the solid $Mg(OH)_2$ product on the MgH_2 surface prevents further reaction. Therefore, acetic acid is added to make soluble magnesium acetate (reaction 6), which allows reaction to occur with the inner layers as the reaction front moves deeper into the MgH_2 solid.^{15,16}



To study the hydrogen production during hydrolysis of MgH_2 in the presence of acetic acid, initially, the pinch clamp/stopcock is shut off to the fuel cell so that the hydrogen produced is directed toward the sensor. The MgH_2 (VWR International) sample with the mass 100–150 mg (the MgH_2 is a limiting reagent and water is in excess) is placed inside the dry flask and capped with a septum stopper. The 5.0 mL of 2.0 wt % acetic acid is added using a syringe and needle through the septum stopper to ensure that the hydrogen produced in reaction 6 is not released to the surroundings.

The volume of the gas law syringe is kept constant during the hydrolysis. The pressure/temperature sensor plugs into a PASPORT USB Link, PS-2100A, which connects to a computer's USB port for data collection. The DataStudio software¹⁷ is fully compatible with the PASPORT sensor, and displays may include digits, graphs, meters, and tables. For example, a plot of pressure versus time data may be displayed on the computer.

Fuel cell consumption of hydrogen during hydrolysis of MgH_2 in the presence of acetic acid is measured. After the hydrolysis, the pinch clamp/stopcock to the fuel cell is opened to allow the hydrogen to reach the fuel cell, and measurements are recorded of current, voltage, and time the motor is running.

Hydrogen storage capacity of MgH_2 is determined by thermogravimetric analysis (TGA). TGA of the MgH_2 sample is provided to the students by the instructor to determine the weight loss when hydrogen is released with an increase in

temperature. TGA was conducted in an atmosphere of gaseous nitrogen. A sample of the magnesium hydride with the mass 25.617 mg was heated in a platinum crucible with a temperature rate of 20 °C/min up to 500 °C and held at isothermal conditions for 2 min. The weight loss analysis showed that the sample lost 3.50 mass % by 375 °C. The weight loss corresponds to the actual hydrogen capacity of the sample used in this study.

HAZARDS

Hydrogen is the lightest of the elements and therefore dissipates rapidly in open areas and migrates through very small spaces. It normally is present only in the gaseous state since its boiling point is -252 °C. Hydrogen should be stored safely and effectively. The immediate dangers are of fire or explosion in enclosed environments. Sensors often are installed to detect concentrations of hydrogen approaching 4%; the lowest percentage in the atmosphere at which ignition can occur, referred to as the 100% lower explosion limit (LEL).

The septum stopper should not be wired onto the 24/40 joint of the flask since it serves as a potential pressure vent in case of the buildup of high pressure. Granular Zn should be used, never powdered Zn. MgH_2 should be stored in a desiccator to avoid contact with water, and a dry flask should be used for the reaction. Take care when using the syringe since accidental needlesticks may cause infection.

EXPERIMENTAL RESULTS AND DISCUSSION

Experiment 1a: Hydrogen Storage Capacity of Hydrochloric Acid via Reaction with Zinc

Table 1 was created from voltage and current readings of the fuel cell when hydrochloric acid was reacting with granular Zn. The data were collected during the first 10.5 min of the reaction, which was far from completion.

When the data for the time of the running motor, t in seconds, voltage, and current were collected, the moles of hydrogen consumed by the fuel cell were calculated for each step using eq 7, where n is the number of moles of electrons transferred (two per mole of hydrogen), and F is Faraday's constant (96,485 C/mol).

$$\text{Mass of hydrogen gas consumed} = (I)(t)(\text{Molar Mass}_{H_2})/(nF) \quad (7)$$

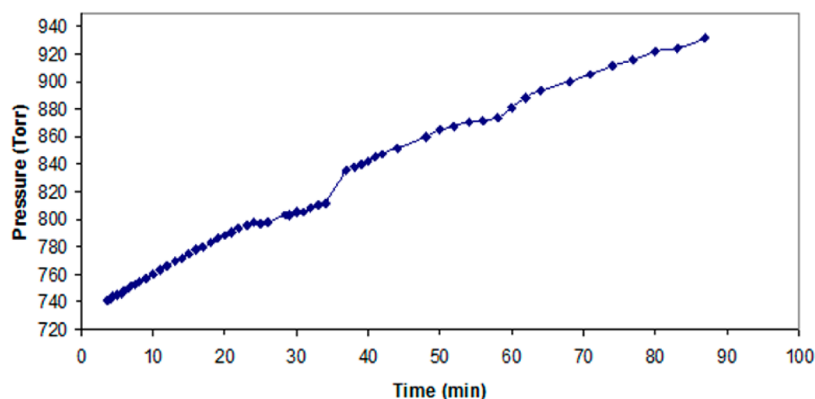


Figure 3. Plot of total pressure as a function of reaction time for 149.7 mg of MgH_2 with 5.0 mL of 2.0 wt % acetic acid.

The voltage and current at each measurement time consistently were about 0.7 V and 0.014 A, respectively, for a power of 0.01 W. Power was calculated from the product of voltage V in volts and current I in amps.

The reaction of 2.0 g of Zn with 8.8 mL of 3.0 M HCl, where HCl is the limiting reagent, would theoretically produce 0.027 g of gaseous hydrogen. The hydrogen consumption in the fuel cell by the time the measurement was stopped was only 0.34% of the theoretical yield. The calculation based on eq 7 shows that 100% yield of gaseous hydrogen, when the reaction goes to completion, would provide electrical energy to run the 0.01 W motor for about 50 hours.

Experiment 1b: Hydrogen Storage Capacity of Magnesium Hydride

The reaction of 149.7 mg of MgH_2 with 5.0 mL of aqueous 2.0 wt % acetic acid results in a nearly linear increase in the pressure as a function of reaction time when the measurement was discontinued at 90 min, far from completion (Figure 3).

The average rate of hydrolysis, which was calculated using the ideal gas law to convert pressure to moles, was found to be $(3.7 \pm 0.2) \times 10^{-7} \text{ mol H}_2 \text{ s}^{-1}$. Calculations show that after 90 min duration of the reaction, the mass loss of the MgH_2 sample is 2.3%. To calculate moles of hydrogen released and convert them to grams, the volume of the system was needed. Assuming ideal gas behavior for a fixed amount of hydrogen, the volume of the system in Figure 2, V_o , was calculated using eq 8 when the stopcock is turned off toward the fuel cell, and the volume of the syringe was changed from the initial, V_i , to final volume, V_f .

$$(V_i + V_o)/(V_f + V_o) = (T_f P_i)/(T_i P_f) \quad (8)$$

The volume of the system was found to be $110 \pm 8 \text{ mL}$.

Similar to the experiment with HCl, data were collected for the time of the running motor, voltage, and current, and using eq 7, the amount of hydrogen consumed by the fuel cell was calculated. The voltage, current, and power results for the operation of the fuel cell during the MgH_2 experiment were within experimental error of the data reported for the HCl reaction with Zn in Table 1. The hydrolysis of 100.7 and 147.3 mg of MgH_2 with 5.0 mL of 2.0 wt % acetic acid consistently showed a rate of hydrogen consumption of $6.7 \times 10^{-8} \text{ mol s}^{-1}$; the mass of hydrogen consumed by the fuel cell was 0.13% after 78.2 and 47.0 min of reaction time for two samples, respectively.

The actual hydrogen storage capacity of the MgH_2 sample in this experiment was determined by TGA weight loss measure-

ments to be 3.5%. For the fuel cell consumption experiments, the measured weight loss of 0.13% is only 4% on the TGA value, primarily because the reaction was stopped far away from completion, and additionally, a large amount the hydrogen, which is produced, remains in the volume outside of the fuel cell. Calculations show that the actual hydrogen capacity of the MgH_2 samples should be enough for more than 35 h of electricity generation by the fuel cell.

The Supporting Information is provided for the experiments and shows additional figures, sample calculations, and the TGA weight loss for MgH_2 as a function of temperature.

CONCLUSIONS

Hydrogen storage capacity of hydrogen-containing compound experiments were developed for use in workforce training associated with clean energy technologies. Undergraduate students gained valuable experience in (1) examining the production of hydrogen stored in aqueous hydrochloric acid and solid magnesium hydride, (2) consuming hydrogen with a fuel cell, (3) analyzing and comparing the storage capacity of two hydrogen-containing compounds, and (4) making measurements using the ideal gas equation of state.

ASSOCIATED CONTENT

Supporting Information

Detailed descriptions of the experiments are provided for instructors and students showing additional Figures of the experiments, sample calculations, and the TGA weight loss for MgH_2 as a function of temperature. This material is available via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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