



Hydrogen Production: Fundamentals and Case Study Summaries

Preprint

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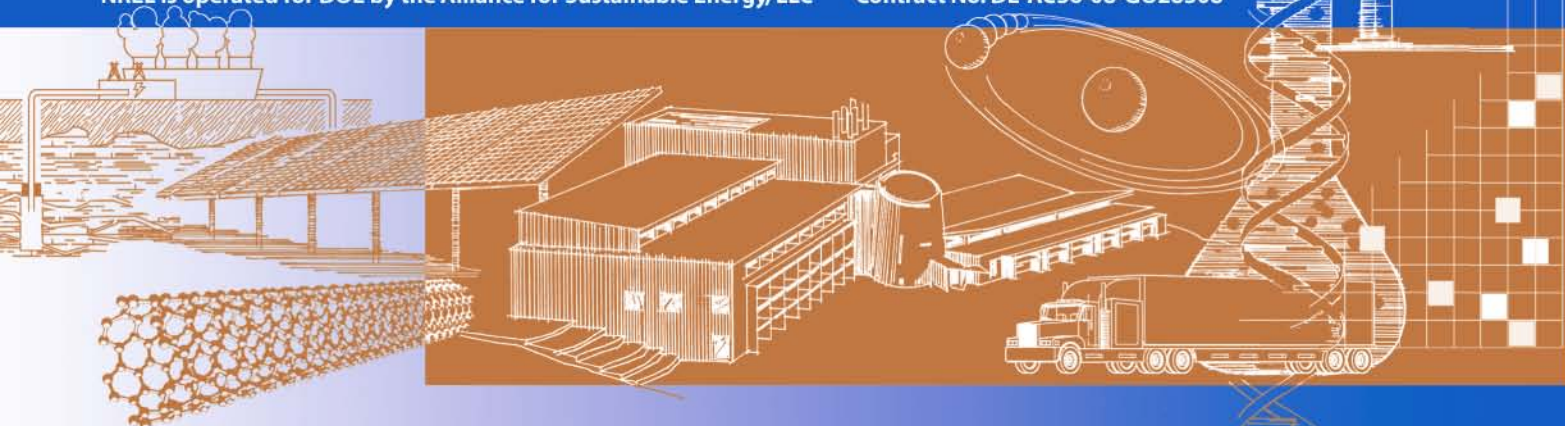
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List of Acronyms and Abbreviations

| | |
|-----------------|--------------------------------------|
| AC | alternating current |
| AC/DC | AC-to-DC |
| atm | atmosphere |
| BEPC | Basin Electric Power Cooperative |
| Btu | British thermal units |
| DC | direct current |
| DC/DC | DC-to-DC |
| DOE | U.S. Department of Energy |
| F | Faraday constant |
| G | Gibbs free energy |
| H | enthalpy |
| HARI | Hydrogen and Renewables Integration |
| HHV | higher heating value |
| IC | internal combustion |
| JANAF | Joint Army-Navy-Air Force |
| kJ | kilojoule |
| kWe | kilowatt electrical |
| kWh | kilowatt hours |
| LHV | lower heating value |
| mol | mole |
| MPPT | maximum power point tracking |
| NREL | National Renewable Energy Laboratory |
| Nm ³ | normal cubic meter |
| NWTC | National Wind Technology Center |
| PEM | polymer electrolyte membrane |
| PV | photovoltaic |
| RE | renewable energy |
| S | entropy |
| V | volt |
| Wind2H2 | Wind-to-Hydrogen project |

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Heating Value, Heat of Reaction, and Free Energy

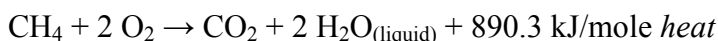
One of the issues that arises when discussing the calculation of the electrical efficiency of a fuel cell or an electrolysis cell is confusion about the terms heat of combustion (often called the heating value), the heat of reaction, the heat of formation, the free energy of reaction, and the free energy of formation. Hydrogen and hydrocarbon fuels also pose a source of confusion about whether the water vapor produced during combustion is condensed back into liquid water or is lost as a vapor diluted in the combustion products. Condensing the water vapor produces additional heat. Finally, there is confusion about standard conditions.

Total energy is composed of both electrical and thermal energy known as enthalpy (H). The amount of electrical energy is known as the Gibbs free energy (G) and corresponds to the maximum amount of useable electrical energy available when hydrogen recombines with oxygen. Irreversible energy or entropy (S) is the “cost of doing business” and is dependent on the temperature at which the reaction takes place. The loss due to entropy is similar to how a bouncing ball loses energy when hitting the floor, as friction from the action of bouncing causes a transfer of thermal energy to atoms in the floor. The energy transferred to those floor atoms dissipates and is not recoverable. Consequently, the change (Δ) in these quantities from a standard set of conditions follows the form shown below.

$$\Delta H = \Delta G + T\Delta S$$

Heat of Combustion and Heat of Reaction

By definition, the heat of combustion is the amount of heat released when 1 gram molecular weight of a substance is burned in oxygen. (Heat of reaction is a more generic term and refers to the heat released in any chemical reaction, combustion or otherwise.) Heat of combustion measurements usually are made in a calorimeter under controlled conditions in which the water vapor, if produced, is condensed and the additional heat of condensation is included. The heat of combustion of methane, for example, is 890.3 kilojoule (kJ) per mole when measured at 25°C in a calorimeter.



If the water vapor produced is not condensed, then the heat of combustion of methane is 802.3 kJ/mole, with the difference being the latent heat of condensation of the water vapor. The greater value—based on forming liquid water—is known in the industry as the higher heating value (HHV) of methane. The lesser value—based on forming water vapor—is the lower heating value (LHV) of methane. Most standard natural gas appliances (e.g., water heaters, gas furnaces, gas ranges) operate with an excess of air, and the water vapor does not condense but remains dissolved in the exhaust stream. This also is true of internal combustion engines and gas turbines. In the United States, however, the efficiencies of appliances and heat engines usually are rated based on the HHV, whereas in European communities LHV is used. The use of LHV in calculating heat engine efficiencies yields greater efficiency numbers than those using HHV.

Standard Conditions

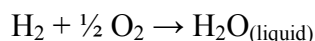
The heat of combustion changes with temperature. For example, the heat of combustion of methane (LHV) at 1,000 K (727°C or 1,340°F) is 800.9 kJ/mole, which is slightly less than the LHV value of 25°C. It is helpful, therefore, to use a standard set of conditions for calculating

efficiency. The usual practice in chemical thermodynamics is to choose 1 atmosphere (atm) pressure and 25°C (298 K), although other conditions are used as standards by different industries and in other parts of the world.

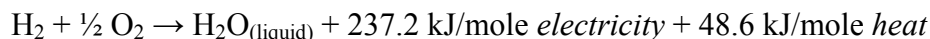
Free Energy

There are two definitions of free energy and both are related to work done by the system. The Helmholtz free energy is the maximum amount of work that can be obtained from a system under perfectly reversible conditions, and is used with thermodynamic calculations of heat engines. Gibbs free energy is the net work that can be done by a system. In an electrochemical cell working reversibly at constant temperature and pressure, the net work is equal to the electrical work. Because we want electrical work, the Gibbs free energy is important to fuel cell calculations.

Heat is released in the combustion of hydrogen in oxygen. In the electrochemical reaction between hydrogen and oxygen in a fuel cell, electricity and heat are produced. Although the chemical equation is written the same way for both reactions, the energy values are not equal. The heat produced by combustion does not equal the electricity produced in the fuel cell.



The HHV for the combustion of hydrogen is 285.8 kJ/mole, but the Gibbs free energy for the reaction—and therefore the maximum electricity produced by a fuel cell—is only 237.2 kJ/mole. The difference, 48.6 kJ/mole, appears as heat produced in the fuel cell. We can show this by the following equation for the fuel cell reaction.



In sum, all fuel cells operating on hydrogen and oxygen produce heat in addition to the electricity. The distribution of energy produced between electricity and heat shown above, however, is for a perfect fuel cell operating in a thermodynamically reversible manner. Actual, practical fuel-cell devices incur losses due to inefficiencies of the electrochemical reactions and due to electrical and ionic resistance as the current flows through the fuel cell. These generically are classed as internal resistance losses, and manifest as additional heat produced by the fuel cell at the cost of the electrical generation. Nevertheless, the sum of the electricity and the heat produced by the fuel cell must equal the HHV (or LHV, if the water vapor produced is not condensed).

Heat of Formation and Free Energy of Formation

The definition of the heat of formation is the heat released or required when chemicals are formed from their elements in their standard state. The heat of formation of the elements in their standard state is, by definition, zero.

The equation for the formation of methane from its elements is given below.



The heat of formation for this reaction at 25°C is listed in the Joint Army-Navy-Air Force (JANAF) Thermodynamic Tables as -74.9 kJ/mole. The minus sign indicates that the methane

contains less energy than the elements do, and that heat would be released by this reaction were it possible to cause the reaction under standard conditions. Likewise, the free energy of formation of a compound is the work that could be recovered from a reaction in which the compound is formed from its elements under standard conditions.

In the unique case of hydrogen reacting with oxygen to form water, the heat of formation of water has the same values as the heat of combustion of the hydrogen. This is true only because, in the combustion reaction, water is formed from its elements. This is a unique situation that is shared by only a few other chemical reactions. Although the numerical values are the same, the concepts of the heat of formation and the heat of combustion are distinctly different. In the discussion that follows, we will use the heats of combustion, HHV and LHV, without further reference to heat of formation or the heat of reaction.

Calculating Fuel Cell System Efficiency

The standard method for calculating the efficiency of a fuel cell power plant or other electrical generation device is to divide the electricity produced by the HHV of the fuel used. This is a reasonable method for calculating power plant efficiency, because the power-plant operator purchases fuel (natural gas is sold by heating value) and sells electricity.

$$\text{Electrical Efficiency} = \frac{\text{Electricity produced}}{\text{HHV of fuel used}}$$

Therefore, there is a maximum theoretical limit to the electrical efficiency attainable by a fuel cell system represented by the Gibbs free energy divided by the heat of combustion of the fuel. In the case of the hydrogen fuel cell this value is the Gibbs free energy/HHV (237.2 kJ/mole/285.8 kJ/mole = 83%). The use of HHV here is in keeping with the method used in the United States to calculate efficiency for internal combustion (IC) engine/generators and gas turbine/generator systems.

Some U.S. developers of high-temperature fuel cells, however, prefer the European convention and instead use the LHV of hydrogen for efficiency calculation. The JANAF Tables list the Gibbs free energy for the formation of water vapor from hydrogen and oxygen as 228.6 kJ/mole, so the maximum theoretical efficiency of a complete fuel cell system based on LHV of hydrogen is 228.6 kJ/mole/241.8 kJ/mole or 94.5%. Using the LHV convention for calculating the efficiency of an electrical generator always yields numbers greater than those yielded by calculations using the HHV for the same system. When quoting electrical efficiency of an electric generator it is important to indicate whether it is based on the HHV or the LHV calculation method.

Practical fuel cells cannot achieve these maximum electrical efficiency numbers because of internal resistance losses. For example, a practical fuel cell operating near its maximum power output might be able to produce only 154 kJ of electricity per mole of hydrogen consumed, with the rest of the heating value appearing as heat produced by the fuel cell. The calculation for such a fuel cell is: 154 kJ/mole/285.8 kJ/mole = 54% efficient (HHV). The remaining 46% of the energy produced can be recovered from the fuel cell system as co-generated heat.

Voltage Efficiency of Fuel Cells and Stacks

The electrical system efficiency calculations discussed above are applied globally to complete fuel cell systems that include many individual components, such as fuel processors, humidifiers, fuel cell stacks, power conditioners, and controls. Many experimenters and developers, however, also wish to assess the efficiency of the fuel cell stack separate from the efficiency of the system. For this reason it is convenient to use the concept of voltage efficiency, which is defined as the actual cell (or cell stack) operating voltage divided by the thermodynamic cell voltage.

$$\text{Voltage efficiency} = \frac{\text{Operating voltage (V)}}{\text{Thermodynamic voltage (E)}}$$

The thermodynamic cell voltage can be calculated using the Gibbs free energy and the Nernst equation.

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[H_2O]}{[H_2][O_2]^{1/2}}$$

Where:

- E = the thermodynamic voltage under prevailing conditions
- E° = the thermodynamic voltage under standard conditions
- R = the gas constant (8.314 J deg K⁻¹ mole⁻¹)
- T = temperature in degrees Kelvin (25°C = 298 K)
- n = the number of electrons transferred (2 in this case)
- F = Faraday constant (96,485 Coulomb mole⁻¹)
- $[]$ = the thermodynamic activity of the reactants and products, which, for gases, can be approximated by their partial pressure in atmospheres.

Gibbs free energy can be converted into a thermodynamic voltage using the formula in which free energy is in joules per mole, as shown below.

$$\text{Gibbs free energy (standard conditions)} = nFE^\circ$$

Under standard conditions, the Gibbs free energy for the hydrogen-oxygen reaction is 237.2 kJ/mole for the production of liquid water at 25°C. Therefore, the thermodynamic voltage for a hydrogen-oxygen fuel cell operating at standard temperature and pressure is 1.229 volts.

$$E^\circ = \frac{237,200 \text{ J}}{2(96,485)} = 1.229 \text{ V}$$

The Nernst equation is useful for calculating the thermodynamic voltage at varying pressures and reactant concentrations, but it should be noted that the Gibbs free energy of the hydrogen/oxygen reaction changes with temperature. Therefore, to calculate the thermodynamic voltage of a cell at a temperature other than standard temperature requires looking up the Gibbs free energy for the reaction at that temperature in a thermodynamic table. For example, the thermodynamic voltage for a high-temperature fuel cell operating on hydrogen/oxygen at atmospheric pressure at 1,000 K is 0.998 volts. Experimenters and developers of higher-temperature fuel cells typically use the

free energy for the formation of water vapor rather than liquid water in their calculations. Both are listed in most thermodynamic tables.

A good fuel cell with well-sealed components and a properly functioning electrolyte should exhibit a voltage close to the thermodynamic voltage when it is not producing power (no load). This is also known as the open-circuit voltage. Thus, a fuel cell operating at 25°C with 1 atm of hydrogen at the anode and 1 atm of pure oxygen at the cathode should exhibit a voltage of 1.23 volts with no load. Comparison of the actual open-circuit voltage with the thermodynamic voltage can be used to determine the integrity of the cell. Pinholes in the electrolyte that allow fuel and oxidant to mix, for example, reduce the open-circuit voltage and indicate a problem.

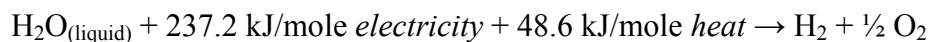
The approximate efficiency for a fuel cell stack that is producing electrical power can be calculated by dividing the operating voltage by the thermodynamic voltage. Thus, a polymer electrolyte membrane (PEM) fuel cell operating at 0.800 volts under standard conditions has a voltage efficiency of $0.800 \text{ V} / 1.229 \text{ V} = 65\%$.

Other Efficiency Calculations

Another calculation that often is used to describe fuel cell stack performance is fuel cell stack efficiency, which is calculated as the direct current (DC) electrical output of the fuel cell stack divided by the LHV of the fuel consumed in the stack. This calculation is similar to the global system efficiency calculation, except that parasitic electrical losses due to auxiliary systems are not included in the calculation and the LHV of the fuel used by the stack does not include parasitic fuel use upstream or downstream of the fuel cell. It also is a more difficult calculation to perform because accurate measurements of the amount of fuel consumed by the fuel cell stack are not easy to obtain.

Water Electrolysis

Water electrolysis is the reverse of the fuel cell reaction. In fact, many fuel cells based on PEM and solid-oxide technology can work both as a fuel cell or a water electrolysis cell, depending on the direction of the electrical current. The equation for the water electrolysis reaction simply is the reverse of the fuel cell equation.



The efficiency calculations, therefore, can be inverted as well. The efficiency of an electrolysis system, for example, can be calculated as the heating value of the hydrogen produced divided by the electrical energy input.

$$\text{Electrical efficiency}_{(\text{HHV})} = \frac{\text{HHV of } \text{H}_2 \text{ produced}}{\text{Electricity used}}$$

or

$$\text{Electrical efficiency}_{(\text{LHV})} = \frac{\text{LHV of } \text{H}_2 \text{ produced}}{\text{Electricity used}}$$

Other efficiency measures often are listed on the product brochures of electrolyzer manufacturers, the most frequently used being kilowatt hours (kWh) per normal cubic meter (Nm³) of dry hydrogen produced (kWh/Nm³). The kilowatt-hours per kilogram term also appears frequently in the literature. These measures have more meaning to the customers of electrolysis units who, after all, want hydrogen gas and not heat.

Voltage Efficiency of Electrolysis Cells and Stacks

A problem exists, however. Using this approach to calculate the maximum thermodynamic efficiency of an electrolysis cell operating reversibly produces nonsense numbers that exceed 100%.

$$(\text{HHV}) \ 285.8 \text{ kJ/mole} / 237.2 \text{ kJ/mole} = 120.5\%$$

$$(\text{LHV}) \ 241.8 \text{ kJ/mole} / 228.6 \text{ kJ/mole} = 105.8\%$$

The problem is that it takes both electricity and heat to split water electrochemically and the heat is not being included in the above calculation of the energy input.

Although the thermodynamic voltage for splitting water under standard conditions is the same 1.229 volts as the fuel-cell reaction, practical electrolysis cells—like fuel cells—do not operate near this voltage. Whereas the practical fuel cell operates well below 1.23 volts (in the range of 0.750 to 0.900 volts), the practical electrolysis cell operates above this voltage in the range of 1.60 to 2.00 volts. System efficiencies of practical systems calculated using the above approach, although inflated, always are less than 100%; therefore, the problem is not obvious. It is when we attempt to develop a method for calculating individual cell and multiple cell stack efficiency that we see the problem.

Splitting a mole of liquid water to produce a mole of hydrogen at 25°C requires 285.8 kJ of energy—237.2 kJ as electricity and 48.6 kJ as heat; there is no way around this fact. In PEM and alkaline electrolysis cells the heat requirement is supplied from the extra heat generated, due to internal resistance as the electric and ionic currents flow through the cell. This heat requirement is directly traceable back to the electricity supplied. In other words, 285.8 kJ—not 237.2 kJ—of electricity is the minimum required to split water in these cells. This translates into a cell voltage of 1.481 volts, not the 1.229 volts used in calculating the theoretical maximum electrical efficiency of a fuel cell.

The electrochemical potential (standard potential) corresponding to the HHV is 1.481 V/cell as shown below. This represents the thermoneutral voltage at which hydrogen and oxygen are produced with 100% thermal efficiency (i.e., no waste heat produced from the reaction). This is determined using Faraday's Law, and dividing the HHV (285,840 J/mole) by the Faraday constant ($F = 96,485 \text{ coulombs mole}^{-1}$) and the number of electrons needed to create a molecule of hydrogen ($z = 2$).

$$E_o = \frac{\Delta_f H^\circ}{zF} = \frac{285,840 \frac{\text{J}}{\text{mol}}}{2 * 96,485 \frac{\text{C}}{\text{mol}}} = 1.481 \frac{\text{Volts}}{\text{cell}}$$

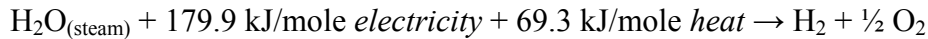
This voltage, 1.481 volts, is required for splitting liquid water. It is the voltage at which an electrolysis cell operating at 25°C can operate without producing excess heat. (Practical cells operate above this voltage and produce excess heat.) It also is the voltage that corresponds to the HHV of hydrogen and therefore represents a more reasonable value to use when calculating cell and stack voltage efficiency. The formula for calculating the voltage efficiency of a cell or cell stack thus becomes the following.

$$\text{Voltage efficiency} = \frac{\text{Thermal neutral voltage (E)}}{\text{Cell operating voltage (V)}}$$

A similar calculation can be performed for water vapor using the LHV. The thermoneutral voltage for splitting water vapor at 25°C is 1.253 volts.

Steam Electrolysis and High-Temperature Cells

The above discussion applies primarily to electrolysis cells operating at temperatures that are less than the boiling point of water; these include the PEM and alkaline electrolysis cells. There is a class of high-temperature steam electrolysis cells under development, however, that operates in the 800° to 1,000°C temperature range, where the thermodynamics are significantly different. As the temperature climbs, the LHV of hydrogen increases and the Gibbs free energy decreases. At 1,000°C, for example, the LHV of hydrogen is 249.2 J/mole and the Gibbs free energy for the reaction is 179.9 kJ/mole. The water-splitting reaction at 1,000°C can thus be written as follows.



The thermodynamic voltage for this reaction—which corresponds to both the open-circuit voltage for the solid oxide fuel cell and the solid oxide electrolyzer cell—is 0.932 volts. The thermoneutral voltage for the electrolysis reaction is 1.291 volts. These high-temperature cells are considerably more efficient in that they have lesser internal resistance losses and improved reaction kinetics as compared to their low-temperature PEM counterparts.

It is well within the realm of possibility that a practical high-temperature electrolysis cell could operate below the thermoneutral voltage. In this case, the heat requirement must be made up by an external heat source. A high-temperature electrolyzer operating at 1,000°C and 1.200 volts, for example, would not generate sufficient heat via internal resistance to keep the electrochemical reaction going. As the cell operated, the electrochemical reaction would withdraw heat from the cell components and cool the cell to the point that it ceases operating. Therefore, to maintain temperature, sensible heat must be supplied to the cell components from an outside source.

In the high-temperature case, calculating the voltage efficiency of the cell can be straightforward and the thermodynamic voltage can be used. In the case of global system efficiency, however, both the electrical input and the heat input from the external source must be included, otherwise the calculation produces a nonsensical answer and an efficiency that is greater than 100%.

$$\text{Voltage efficiency}_{(\text{cell})} = \frac{\text{Thermodynamic voltage (E)}}{\text{Operating voltage (V)}}$$

$$\text{Electrical efficiency}_{(\text{system})} = \frac{\text{HHV of } H_2 \text{ produced}}{\text{Electricity used} + \text{Heat supplied}}$$

Recommendations

The following quote is drawn from a 2002 publication on hydrogen by the Bellona Foundation, of Oslo, Norway. “When calculating the efficiency in a fuel cell, the lower heating value is used. In the electrolysis process, the high heating value is used.” The full report is available at http://bellona.org/filearchive/fil_Hydrogen_6-2002.pdf, and it basically sums up the European point of view.

In the United States, however, the situation is more equivocal. Developers of natural gas fuel cells do use LHV. Gas turbine manufacturers and manufacturers of IC engine generator sets, however, use HHV to calculate electrical efficiency. These groups complain that comparisons of fuel cells with heat engines are unfair because of the different basis used for the efficiency calculations. In the United States, natural gas is sold by the therm (1 therm = 100,000 Btu), but it is measured by the cubic foot. The conversion from cubic feet to therms used by a gas supplier in billing customers uses either the measured gas composition and the sum of the HHV of each fractional component, or the actual calorimeter measurements of the HHV of the gas supplied to the customer. In either case, the customer pays based on the HHV of the gas used. It therefore makes sense that calculations of system efficiency for all electric generators should use the HHV of the fuel.

Electrolyzer manufacturers appear to have standardized on kWh/Nm³ or kWh/kg as a measure of system efficiency, which sidesteps the LHV versus HHV controversy. As noted above, Europeans prefer HHV for calculating electrolyzer efficiency on the basis of heating value.

As stated, splitting a mole of liquid water to produce a mole of hydrogen at 25°C requires 285.8 kJ of energy—237.2 kJ as electricity and 48.6 kJ as heat. It then follows that the ratio of reversible free energy potential (1.229 V) over the thermoneutral voltage (1.481 V) is 83%. This represents the highest efficiency attainable when using the LHV to determine stack voltage efficiency. Likewise, the same can be said for electrolyzer system efficiency calculations. Therefore, it is worth stating that the highest attainable efficiency is 83% when referencing electrolyzer system and stack efficiencies to the LHV.

The HHV easily is converted into more common forms of the higher heating value.

$$285,840 \frac{\text{J}}{\text{mol}} * \frac{1 \text{ mol } H_2}{2.0158 \text{ g}} * \frac{1,000 \text{ g}}{1 \text{ kg}} = 141,799,781 \frac{\text{J}}{\text{kg}} = 141.8 \frac{\text{MJ}}{\text{kg}}$$

$$141.8 \frac{\text{MJ}}{\text{kg}} * \frac{1 \text{ watt} - \text{sec}}{\text{J}} * \frac{1 \text{ kW}}{1,000 \text{ w}} * \frac{1 \text{ h}}{3,600 \text{ sec}} = 39.4 \frac{\text{kWh}}{\text{kg}}$$

The U.S. Department of Energy (DOE) Fuel Cell Technologies Program Multi-Year Plan [1] includes targets for distributed water electrolysis and for central wind water electrolysis using three measures of efficiency: HHV, LHV, and kWh/kg. It also sets goals [2]. In all other hydrogen-production schemes, however—for example in natural gas reforming and biomass gasification production scenarios—“energy efficiency is defined as the energy in the hydrogen

produced (on a LHV basis) divided by the sum of the feedstock energy (in LHV) plus all other energy used in the process.” [3]

Case Studies of Wind/Hydrogen Projects

Canada

Ramea Island

Ramea Island is a small island located in the Atlantic Ocean off the Southern coast of Newfoundland and Labrador in eastern Canada. It was the site of Canada’s first wind-diesel demonstration project, in 2004. In an attempt to increase the proportion of the island’s electrical generation coming from wind, a project to integrate hydrogen storage to the existing wind-diesel system was initiated. The system consists of three new 100-kW turbines in addition to the six existing 65-kW wind turbines and a 90 m³/h alkaline electrolyzer with 2000-m³ hydrogen storage (10 bar). The stored hydrogen will be converted back to electricity, as need be, via four 62.5-kW hydrogen internal combustion engine generators. All system components are now delivered to this remote location with integration efforts underway.

Prince Edward Island

Prince Edward Island is home to Canada’s Wind Energy Institute and boasts one of the strongest wind regimes in Canada with 44 MW installed and another 30 MW planned. The Wind Energy Institute is located on North Cape area of the island and is well positioned to host a wind-to-hydrogen demonstration project.

The system’s components consist of:

- Wind Turbine: Vergnet 60-kW variable speed, or the local grid
- Electrolyzer: Unipolar Alkaline (66 Nm³/h)
- Storage: 4000 Nm³/h (at 17 bar) with plans to add 90 kg at 450 bar
- 120-kW retrofitted diesel genset

This project will provide valuable data, resulting from the direct connection of the variable speed turbine to the electrolyzer. It is also the only ongoing project that currently employs a unipolar alkaline electrolyzer and should provide information about the durability of this type of electrolyzer with variable input.

Aside from the scientifically interesting data that will be generated, the project has a number of applications for the hydrogen that will be produced. Hydrogen is used with a fuel cell as part of a back-up/auxiliary power unit and is also being used to fuel two 12-seat hydrogen internal combustion engine buses. These buses are an integral part of the public transit system in Charlottetown (the provincial capital).

Greece

RES2H2 Project

For the Greek test site of RES2H2, a Casale Chemicals 25-kW electrolysis unit operating at a pressure of up to 20 bar is connected to a 500-kW gearless, synchronous, multi-pole Enercon E40 wind turbine. The electrolysis unit was developed with special cells to be able to withstand

rapid changes of input power (15% to 100% capacity in 1 sec). The electrolyzer operates in various modes (percentage of wind turbine production, “peak-shaving,” etc.), with excess energy from the wind turbine being fed to the grid. The electrolytic hydrogen is purified prior to entering a buffer tank. Part of the produced hydrogen is stored in novel metal hydride tanks having capacities of approximately 40 Nm³ H₂. The rest of the produced hydrogen is compressed to 220 bar and fed to cylinders at a filling station.

Several conclusions were reached from this undertaking:

- Besides meeting technical and cost targets and addressing safety issues, the design of a hydrogen energy system must be done in relation to what is market ready—there is no point to optimizing a system that specifies units having capacity that is not available or that are still at an early development phase.
- The transportation and installation of hardware is something to be considered for such installations that in many cases are remote and have poor access. In terms of size and weight in combination with the poor access road quality, the capacities of the systems involved at the present site were the limit for conventional trucks and lifting equipment.

Spain

RES2H2 Project

A second component of the RES2H2 project is located at the Instituto Tecnológico de Canarias, on Gran Canaria Island, Spain. The project's major components are:

- Wind turbine: 500 kW (ENERCON)
- Electrolyzer: 5 Nm³/h H₂ per 20 bar
- Hydrogen compressor: 7.5 kW per 220 bar.

The goal for this site is to optimize the energy produced by a wind turbine by providing electricity to the grid, and producing drinking water through a reverse-osmosis plant and hydrogen through an electrolyzer (this will be stored in a tank and used in a fuel cell for re-electrification purposes).

ITHER Project

The aim of the ITHAR Project is the start-up of an installation that enables testing of hydrogen generation by electrolysis, using electricity obtained from renewable sources, with the most diverse available technologies. The project tries to cover all of the hydrogen chain (production, management, and efficient use), obtaining the primary energy from renewable sources by means of processes currently available (photovoltaic and wind).

The project consists of three turbines, each with a different type of technology and on an average range of powers (80 kW, 225 kW, and 330 kW). With this infrastructure, it is expected to be pioneering not only in Spain, but also at an international level due to the range of powers handled.

For hydrogen storage, the project includes three metal hydride tanks with a capacity of 7 Nm³ each used to store 100 kWh of energy. In addition to the metal hydride tanks two other options exist, one is to store hydrogen gas at 45 bar in a tank and the second is using a trailer of cylinders

at 200 bar, with a total capacity of 400 Nm³. The hydrogen is used in two Ballard 1.2-kW fuel cells and a Plug Power 5 kW, which are integrated as a back-up system in the building.

Tahivilla Project

This project involves a wind-hydrogen pilot plant located near Cadiz which is a part of a research project led by ENDESA Generation with Green Power Technologies, AICIA, and INERCO as partners. After a preliminary study of electricity production by the wind farm where the pilot plant is located (by comparing the production and prediction curves of the last 3 years), simulations were made to optimize wind energy generation by means of an integrated system of hydrogen and electric energy generation. This system, whose main components are an electrolyzer, a fuel cell, and a hydrogen tank, allows the generation of hydrogen by using part of the energy produced by a variable-speed wind turbine.

The system is located on-site at an 80-MW park in the south of Spain (1,900 equivalent production hours per year, “MADE 800” wind turbines). It is composed of an electrolyzer with a maximum electricity consumption of 41 kWe. After the hydrolysis is complete the resulting oxygen is vented and the hydrogen is stored at medium pressure (15 bar) in a storage tank. The system also has a compressor, for storage at 200 bar, and a fuel cell capable of generating 12 kWe.

United Kingdom

HARI Project

The Hydrogen and Renewables Integration (HARI) project was established in 2001, on the site of an existing renewable energy system at West Beacon Farm, in Leicestershire, England. The two main objectives of this project were to demonstrate and gain experience in the integration of hydrogen energy storage systems with renewable energy systems, and to develop software models which could be used for the design of future systems of this type.

Prior to the installation of the hydrogen energy system, the existing renewable energy systems at the site included two 25-kW wind turbines, 13-kW photovoltaics, and two micro-hydroelectric turbines with combined output of 3 kW. The addition of a hydrogen energy storage system to the existing renewable energy (RE) supply network was seen as a means of balancing the varying supply with the fluctuating demand, and enabling the evaluation of the feasibility of a standalone RE system. Three key components added to the existing network, a 36-kW alkaline electrolyzer (with 25-bar output pressure), 2,856 Nm³ of pressurized (137 bar) hydrogen storage, and 2 fuel cells (2 kW, 5 kW).

During the operation of this site between 2001 and 2006, several lessons were learned, and suggested a number of ways that the overall efficiency could be optimized when designing similar systems. Importantly, matching the output and input requirements of all components ensures the most efficient energy conversion and hydrogen production. Additionally, the power conversion electronics were found to be the most significant parasitic losses in the system. Over time, the electrolyzer module’s efficiency also declined. The variable input from the wind turbine caused the electrolyzer to cycle, which lead to degradation of the stacks. When it was first installed the electrolyzer was rated at 36 kW, but over 2 years this had risen to 39 kW for the same hydrogen output.

PURE Project

The standalone small-size wind hydrogen energy system PURE Project was a joint project of Unst (community of the Shetland Islands), siGEN (system integrator), and AccaGen SA for the PURE Community of Shetland-Islands, and is supported by the European Union. The project aims to demonstrate how wind power and hydrogen technology can be combined to meet the energy needs of a remote rural industrial estate. PURE was conceived to test and demonstrate safe and effective long-term use and storage of hydrogen produced by renewable energy using wind-powered electrolysis of water, and to regenerate the stored energy into electric energy with a fuel cell. The key components of the system are:

- Wind turbines: Two 15 kW (Proven Ltd)
- Electrolyzer: 15 kW alkaline operating at 55 bar (AccaGen SA)
- Hydrogen storage: 44 Nm³ in H₂ cylinders
- PEM fuel cell: 5 kW (Plug Power).

The electrolyzer section consists of an AccaGen electrolyzer unit assembled with advanced cells specifically designed and manufactured by AccaGen SA for wind application, capable of operating up to 55 bar. Apart from high energy efficiency and good dynamic performance in variable operation, a particularly important requirement for a wind-operated water electrolyzer is the possibility of operating the electrolyzer over a wide range with high current yields and sufficient gas purities.

United States

Basin Electric, Wind-to-Hydrogen Energy Pilot Project

The goal of this project was to research the application of hydrogen production from wind energy, allowing for continued wind energy development in remote wind-rich areas and mitigating the necessity for electrical transmission expansion. [4]

Four modes of operation were considered in the feasibility report to evaluate technical and economic merits. It should be noted that all the modes studied represent hydrogen production efficiencies that are less than those achievable if the system were operated at full production on “grid” electricity. The modes of operation studied were:

- Mode 1—Scaled wind
- Mode 2—Scaled wind with off-peak
- Mode 3—Full wind
- Mode 4—Full wind with off-peak.

In summary, the feasibility report, completed on August 11, 2005, found that the proposed hydrogen production system would produce between 8,000 kg and 20,000 kg of hydrogen annually, depending on the mode of operation. This estimate was based on actual wind energy production of one of the North Dakota wind farms of which the Basin Electric Power Cooperative (BEPC) is the electrical off-taker. The cost of the hydrogen produced ranged from \$20 to \$10 per kilogram (again depending on the mode of operation).

The hydrogen-production system utilizes a bipolar alkaline electrolyzer nominally capable of producing 30 Nm³/h (2.7 kg/h). The hydrogen is compressed to 6,000 psi and delivered to an on-site three-bank cascading storage assembly with 80 kg of storage capacity. Vehicle fueling is

made possible through a Hydrogenics-provided gas control panel and dispenser, able to fuel vehicles to 5,000 psi.

A key component of this project was the development of a dynamic scheduling system to control the wind energy's variable output to the electrolyzer cell stacks. The dynamic scheduling system received an output signal from the wind farm, processed this signal based on the operational mode, and dispatched the appropriate signal to the electrolyzer cell stacks.

Unfortunately, chronic shutdown issues prevented consistent operation, and therefore did not allow accurate economic analysis as originally intended. Much valuable experience was gained in the form of "lessons learned," however, and the project served as an extremely valuable platform for educating the public.

National Renewable Energy Laboratory and Xcel Energy, Wind-to-Hydrogen Project

Xcel Energy and the U.S. Department of Energy's National Renewable Energy Laboratory (NREL) have collaborated to design, install, and operate the Wind-to-Hydrogen (Wind2H2) project. As the largest provider of wind-generated electricity in the United States, Xcel Energy is working with NREL to establish and understand state-of-the-art renewable electrolysis equipment and the operation of a renewable hydrogen production facility. Hosted at NREL's National Wind Technology Center (NWTC), the Wind2H2 system was approved for initial operation in March 2007 and is enjoying success as a demonstration project, producing hydrogen directly from renewable energy sources. This unique research-oriented project uses solar and wind energy to produce and store hydrogen. The stored hydrogen can be used both as a transportation fuel and as an energy-storage medium, effectively allowing renewable energy to be stored and then converted back to electricity at a later time.

The Wind2H2 project is helping researchers understand the hurdles and potential areas for improvement in emerging renewable electrolysis technologies. By allowing engineers to operate and configure an integrated electrolysis facility, this project has enabled the investigation and analysis of hydrogen production, compression, storage, and electricity generation. This project is generating valuable data that are being used to improve the designs of future renewable electrolysis systems. The Wind2H2 project provides important guidance to industry and key stakeholders for development of future renewable electrolysis systems. The Wind2H2 project is the only renewable hydrogen production facility in the world that can operate multiple electrolyzers in any of the following configurations:

- Grid connected
- Directly connected from the output of a photovoltaic array to the electrolyzer stack
- Real-time electrolyzer stack current control based on a power signal from a wind turbine
- Closely coupled photovoltaic (PV) and wind energy sources to the electrolyzer stack with custom designed and built power electronics.

NREL and Xcel Energy have undertaken the Wind2H2 project with several key objectives in mind. First and foremost the Wind2H2 project is being used to demonstrate the operation of a renewable electrolysis system, allowing researchers to evaluate actual system performance and costs and to identify areas for cost and efficiency improvements. Additionally, the project

provides operational experience with a renewable electrolysis hydrogen-production facility, enabling project engineers to investigate operational challenges and to explore system-level integration issues and opportunities for performance and cost improvements resulting from system-level optimization. The project investigates how to maximize the use of renewable energy resources in renewable hydrogen-production systems by optimizing energy transfer from photovoltaic arrays and wind turbines to the stacks of commercial electrolyzers. Finally, the project is designed to explore operational challenges and opportunities related to energy storage systems and their potential for addressing electric system integration issues inherent with high penetrations of variable renewable energy resources.

To help enable greater penetration of renewable energy sources, hydrogen production from renewable electrolysis must be cost-competitive. DOE has a target of reducing the cost of central production of hydrogen from wind-based water electrolysis to \$3.10/kg by 2012; by 2017 DOE seeks to reduce this cost to less than \$2/kg. [1] Electrolyzer manufacturers are improving performance and reducing the capital cost of electrolyzer systems. At the same time, the complete renewable electrolysis system—including the renewable power source, electrolyzer, and interfacing power electronics—must be integrated and optimized to improve system performance and to reduce costs. The Wind2H2 project presents an excellent research platform to investigate these integration and optimization opportunities.

To achieve the objectives of the Wind2H2 project, NREL engineers have been working to complete a number of project tasks. These tasks include:

- Designing, building, and testing dedicated wind- and PV-to-electrolyzer stack power electronics to more closely integrate the renewable energy resources and electrolyzer stacks
- Modeling and simulating renewable electrolysis system performance to enable improved hydrogen-production system designs
- Characterizing renewable energy system impacts on commercial electrolyzer technology and the ability to accommodate the varying energy input from wind and PV sources
- Sequencing multiple electrolyzer systems to improve overall system efficiency, responsiveness, and performance with varying renewable energy sources.

The challenge of renewable electrolysis is designing and implementing systems that can produce hydrogen from renewable sources in a cost-effective way using streamlined, robust, and efficient processes. When the wind turbine or solar array is co-located with the electrolysis system, more direct connection between the source and the electrolyzer stack is possible. This close-coupling eliminates the need for long-distance transportation of electricity and reduces the number of electrical conversions, resulting in a more efficient, cost-effective system.

Valuable operational experience is shared through testing, daily operations, and troubleshooting the Wind2H2 system. Equipment errors are logged to help evaluate the reliability of the system. The valuable lessons from this system operational experience will lead to improved design, implementation, and operational plans of renewable electrolysis systems. For example, integrated renewable electrolysis systems require that system components from different manufacturers be configured to function together smoothly. Consequently, programmable logic

control systems must be able to communicate with all major elements of the system (e.g., electrolyzers, compressors, power converters, load-transfer switches).

As another primary goal of the project, NREL engineers investigated methods to maximize renewable energy use and to optimize energy transfer within the system. Such system-optimization efforts can significantly reduce the cost of renewable hydrogen. In an analysis of the potential improvements to a wind-electrolysis system, project engineers estimated that optimized power electronics would result in a cost improvement of 7%—reducing the cost of hydrogen produced from wind to \$5.83/kg from a baseline of \$6.25/kg. For reference, DOE has set a target for reducing the cost of central production of hydrogen from wind-based electrolysis to \$3.10/kg by 2012. To investigate such optimization opportunities, NREL developed multiple power-electronics configurations that convert varying electricity from a solar PV array and wind turbines into the electricity used by the electrolyzer stacks directly. These power converters have the added benefit of executing maximum power point tracking (MPPT) from the wind turbine or PV array to enable greater energy transfer to the electrolyzer stack.

The PV array connected to the electrolyzer stack both with and without an intermediary power converter was tested and analyzed. The PV array was configured to supply different input voltages to a step-down, DC-to-DC (DC/DC) power converter over many days of testing. We found that using the power converter increases the energy delivered to the electrolyzer stack by 10% to 20%, depending on the PV array input voltage to the power converter. The efficiency of the power converter decreased as the input voltage from the PV array increased. The greatest input voltage from the PV array to the power converter still provided the maximum energy capture to the electrolyzer stack. In other words, although this configuration has the greatest difference between the PV voltage and electrolyzer stack voltage (ΔV), it provided the most energy to the stack over a given day.

A 10-kW wind turbine was connected to one of the PEM electrolyzer stacks through an MPPT alternating current to direct current (AC/DC) power converter. This configuration represents a non-grid-tied (i.e., stand-alone) configuration closely coupling a wind turbine to the electrolyzer stack. Testing and analysis shows that the AC/DC converter has the ability to both maintain optimal operation of the turbine and deliver power to the electrolyzer stack without a battery link. It eliminates several power electronics conversions inherent in grid-tied electrolyzer configurations as well as a battery and its associated maintenance. This AC/DC power converter is undergoing upgrades expected to further increase the energy capture from the wind turbine.

One of the major tasks going forward is to determine how the findings of the Wind2H2 project can improve performance and reduce the cost of renewable electrolysis production systems. The results of system-optimization efforts, performance measurements, and evaluation data will be used in economic models to better understand how these system improvements can reduce the cost of hydrogen produced via renewable electrolysis.

Summary

It is important that parties interested in hydrogen technologies standardize methods of evaluating the performance and efficiency of these technologies. A detailed description of the chemical and electrical processes for electrolysis and fuel cells is presented. Important terminology, units of

measure, constants, and chemical reactions are discussed. Recommendations for calculating electrolyzer and fuel cell performance are suggested.

As interest grows about using hydrogen for grid energy storage and as a transportation fuel, pilot projects and research efforts are underway to experiment with hydrogen production and utilization technologies. The focus of many of these projects is coupling wind energy with hydrogen production (via water electrolysis) in an effort to use all available wind energy and to store that energy to be used during times of high electricity demand. The body of knowledge and lessons learned from designing and operating renewable electrolysis plants is growing. As interested parties learn more about the best way to utilize hydrogen as an energy carrier, the cost of hydrogen produced from renewable sources is decreasing.

References

1. U.S. Department of Energy. "Hydrogen, Fuel Cells & Infrastructure Technologies Program: Multi-Year Research, Development and Demonstration Plan." Office of Energy Efficiency and Renewable Energy. www.eere.energy.gov/hydrogenandfuelcells/mypp/. Accessed December 27, 2009.
2. U.S. Department of Energy. "Hydrogen, Fuel Cells & Infrastructure Technologies Program: Multi-Year Research, Development and Demonstration Plan." Office of Energy Efficiency and Renewable Energy. www.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/production.pdf, Table 3.1.4, footnote f; and Table 3.1.5, footnote e. Accessed December 29, 2009.
3. U.S. Department of Energy. "Hydrogen, Fuel Cells & Infrastructure Technologies Program: Multi-Year Research, Development and Demonstration Plan." Office of Energy Efficiency and Renewable Energy. www.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/production.pdf, Table 3.1.2, footnote f; Table 3.1.8, footnote g. Accessed December 29, 2009.
4. Rebenitsch et al. "Wind-to-Hydrogen Energy Pilot Project: Basin Electric Power Cooperative." www.osti.gov/bridge/servlets/purl/951588-ejIotC/951588.pdf. Accessed December 29, 2009.

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