

Standard Operating Procedure (SOP)

Comparison Metrics and Terms for Low Temperature Electrolysis

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Revision History

This page documents the revisions over time to the SOP. The most recent iteration should be listed in the row space, with consecutive versions following.

Date of Revision	Page(s)/Section(s) Revised	Revision Explanation
04/19/2019	All	First Release
09/24/2019	All	Formatting, clarification of definitions and calculations

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3. Procedures

a. Scope and Applicability

The purpose of this SOP is to define a standard set of definitions, metrics, units, and conventions for low temperature electrolysis (LTE). The goal is to ensure that the literature is consistent from research group to research group, and data is reported in similar formats, such that results can be compared on a similar basis. This SOP is a first draft and is intended to be revised and added to in collaboration with the LTE community.

b. Physical Constants

Constant	Value	Definition/comments
Reversible water vapor splitting potential	1.185 V	Minimum reversible work input excluding heat
Thermoneutral water vapor splitting potential	1.253 V	Used to calculate LHV efficiency
Reversible liquid water splitting potential	1.229 V	Minimum reversible work input excluding heat
Thermoneutral liquid water splitting potential	1.481 V	Used to calculate HHV efficiency

c. Definitions and Acronyms

Below are common acronyms and definitions used in low temperature electrolysis and related characterization methods.

Acronym	Stands for	Definition/comments
AEM	Anion Exchange Membrane	Membrane which selectively conducts anions such as hydroxide
ASTM	American Society for Testing and Materials	A common source for standard test methods
BET	Brunauer–Emmett–Teller	A method for determining surface area
CCM	Catalyst Coated Membrane	One configuration for electrolysis electrodes
DSC	Differential Scanning Calorimetry	A common method for determining membrane thermal stability
ECSA	Electrochemical Surface Area	Catalyst surface area that can be accessed by reactant
FIB	Focused Ion Beam	Method for depth profiling samples
GDL	Gas Diffusion Layer	Electrolyzer component next to the cathode electrode for gas management
HER	Hydrogen Evolution Reaction	Cathode reaction in the electrolyzer
HFR	High Frequency Resistance	Used to determine cell ohmic resistance
HRTEM	High Resolution Transmission Electron Microscopy	High resolution method for characterizing catalysts and other materials

Acronym	Stands for	Definition/comments
HSA	High Surface Area	A relative term used for catalyst supports
ICP	Inductively Coupled Plasma	Method for analyzing trace metals in water
IEC	Ion Exchange Capacity	Measure of membrane conductive sites
LHV	Lower Heating Value	See discussion below
LTE	Low Temperature Electrolysis	Typically less than 100C; liquid water
MA	Mass Activity	Catalyst activity normalized by mass of active material
MW	Molecular Weight	Sum of atomic weights of atoms in molecule
OER	Oxygen Evolution Reaction	Anode reaction in the electrolyzer
PEM	Proton Exchange Membrane	Membrane which selectively conducts cations
PFSA	Perfluorosulfonic Acid	Ionic group in many PEMs, including Nafion™
PGM	Platinum Group Metals	Metals such as Pt, Pd, Ru, Os
PTL	Porous Transport Layer	Electrolyzer component next to the anode catalyst layer, typically the liquid side
RDE	Rotating Disk Electrode	Method for characterizing catalyst activity
SEM	Scanning Electron Microscopy	Method of imaging component features
TEM	Transmission Electron Microscopy	Method of detailed structural imaging
Tg	Glass Transition Temperature	Measure of membrane creep resistance vs. temperature
XRD	X-ray Diffraction	Method to determine catalyst crystal structure

Parameters which are commonly reported differently are hydrogen production rates and efficiency. Discussion of both are included here for clarification.

d. Units of Hydrogen Production

The conventional units for hydrogen production rate vary from region to region and with scale or application. For example, laboratory quantities may be measured in milliliters per minute, while large scale industrial quantities are measured in normal cubic meters per hour or kilograms per day. The table below provides factors for converting between commonly used metrics. It is important to be aware that there is no single standard for “standard temperature and pressure (STP)” conditions or “normal temperature and pressure” conditions. Different agencies within the U.S. government, other national governments, and several international organizations have their own definitions of standard conditions. It is always best to state the reference conditions used for the conversion. The reference conditions for the conversions in the table below are stated in the table, and were selected to be the conditions commonly used for the particular unit in question.

Mass flow rate of hydrogen								
MW			2.016					
g/s	kg/h	kg/day	sccm [S cm ³ /min]	slpm [S L/min]	Nm ³ /h	scfm [S ft ³ /min]	scfh [S ft ³ /h]	
1.000	3.600	86.400	667085	667.085	40.025	25.283	1516.967	
0.278	1.000	24.000	185301	185.301	11.118	7.023	421.380	
0.0116	0.0417	1.000	7721	7.721	0.463	0.293	17.557	
0.00000150	0.00001	0.000130	1.000	0.00100	0.0000600	0.0000379	0.00227	
0.00150	0.00540	0.1295	1000	1.000	0.0600	0.0379	2.274	
0.0250	0.0899	2.159	16667	16.667	1.000	0.632	37.900	
0.0396	0.142	3.417	26385	26.385	1.583	1.000	60.000	
0.000659	0.00237	0.0570	440	0.440	0.0264	0.0167	1.000	
Reference temperature (°C):			0	0	0	20	20	
Reference pressure (kPa):			101.325	101.325	101.325	101.325	101.325	

e. Efficiency

Fundamentally, energy efficiency is measuring the total energy of what is produced as a fraction of the energy input. Energy can enter and exit in multiple forms including chemical fuel, thermal energy, electrical energy, and pressure energy. The energy content of a fuel such as hydrogen is the heat of combustion (or enthalpy of formation of water) as determined by calorimetry. This total energy content is known as the heating value, or the higher heating value (HHV). Conventions develop in any industry for convenience within that industry. The lower heating value (LHV) is a convention that evolved from industries that combust fuels at high temperature. When it was not practical or cost effective to recover all of the energy from the product water vapor, it became convenient to ignore that energy and focus on the energy that the process was utilizing. The lower heating value ignores the energy content of the fuel that went into vaporizing any input or product water, treating all output water as vapor. For low temperature electrolysis, using LHV is equivalent to feeding water vapor as the reactant stream. Use of the lower heating value can be a convenient engineering metric in certain situations, but can become problematic in others. It is largely not problematic when comparing two processes that both take place above 150 °C and use the same fuel (also by convention, many hydrocarbon combustion standards use 150 °C as the threshold temperature rather than 100 °C). Use of LHV can become problematic when comparing processes that use different fuels (as the water content of fuels is different), when comparing processes that have differing abilities to access the energy in the sub-150 °C waste stream, or when comparing a process that takes place above 100 °C to one that takes place below 100 °C.

For hydrogen, the higher heating value is the enthalpy of formation of liquid water (142 MJ/kg, 39.4 kWh/kg, or 286 kJ/mol at 25 °C) and the lower heating value is the enthalpy of formation of water vapor (120 MJ/kg, 33.3 kWh/kg, or 242 kJ/mol at 25 °C). For chemical reactions, the Gibbs energy describes the maximum amount of reversible work that can be extracted from a favored reaction, where ΔH is the enthalpy change, T is the temperature, and ΔS is the entropy change.

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

For the hydrogen-oxygen reaction, the Gibbs energy is 237 kJ/mol when liquid water is the product and 229 kJ/mol when water vapor is the product. Each of these values can be turned into an equivalent potential for the electrochemical reaction (where n = moles of electrons per mole H_2 and F is Faraday's constant), which is a useful reference point and a quick way to assess efficiency.

$$\text{Thermoneutral Voltage } \frac{\Delta H_{HHV}}{nF} = \frac{285,840}{2 \times 96,485} = 1.481 @ 25^\circ\text{C}, 101.325 \text{ kPa}$$

$$\text{Reversible Potential } \frac{\Delta G_{HHV}}{nF} = \frac{237,200}{2 \times 96,485} = 1.229 @ 25^\circ\text{C}, 101.325 \text{ kPa}$$

$$\text{Thermoneutral Voltage } \frac{\Delta H_{LHV}}{nF} = \frac{241,826}{2 \times 96,485} = 1.253 @ 25^\circ\text{C}, 101.325 \text{ kPa}$$

$$\text{Reversible Potential } \frac{\Delta G_{LHV}}{nF} = \frac{228,600}{2 \times 96,485} = 1.185 @ 25^\circ\text{C}, 101.325 \text{ kPa}$$

In the case of the fuel cell reaction, which is a favored reaction, the Gibbs energy can be used to calculate the maximum (ideal) efficiency of the reaction, 83% based on the HHV or 95% based on the LHV. However, for a non-favored reaction such as low temperature electrolysis, the thermoneutral voltage, which corresponds to the energy content of the fuel, represents the maximum possible efficiency. If catalyst and reaction conditions existed to produce H_2 from liquid water at electrochemical potential less than about 1.48 VDC, then energy in some other form such as heat must be supplied to make the total energy input greater than the heating value, or energy would not be conserved.

The cell potential does not tell the whole story of electrolysis efficiency. The other major loss is internal diffusion of hydrogen and oxygen through the membrane. This cross-over represents an efficiency loss whether it fully permeates and leaves the cell or recombines to form water within the cell. Energy was used to split water into hydrogen and oxygen molecules, and some of those molecules won't become useful outputs from the system. It is common to convert the mass flow of permeation into an equivalent current (I_{loss}) or current density (i_{loss}).

The total cell stack efficiency is described by the formula below where the first term is the "voltage efficiency" and the second term is the "current efficiency." Improvements in activation overpotential, membrane conductivity, and mass transport limits generally improve the voltage efficiency. Improvements in membrane conductivity that come from a membrane thickness change are of indeterminate efficiency change without also addressing the current efficiency impacts of increased cross-over. Fundamental decreases in membrane gas permeability lead to an increase in the current efficiency.

$$\eta = \frac{\text{Hydrogen out}}{\text{Electricity in}} = \left(\frac{\Delta H}{2FV} \right) \cdot \left(\frac{I - I_{loss}}{I} \right)$$

With the higher heating value or lower heating value substituted for ΔH , respectively, the formulas become:

$$\eta_{HHV} = \left(\frac{1.481}{V} \right) \cdot \left(\frac{i - i_{loss}}{i} \right)$$

$$\eta_{LHV} = \left(\frac{1.253}{V} \right) \cdot \left(\frac{i - i_{loss}}{i} \right)$$

Both the reversible potentials and the heating values change with temperature and pressure conditions. If predicting a cell voltage at a particular set of conditions, these factors must be considered. However, for efficiency calculations, comparing reactants and products at the reference state is sufficient. Pressurization of the gaseous products (hydrogen or oxygen) through electrochemical compression decreases the voltage efficiency through the Nernst effect and decreases the current efficiency through increased gas cross-over. Pressurization is changing the quality of the hydrogen, generally making it more useful, and the energy put into pressurization should be compared to the energy associated with a competing device doing equivalent compression. When comparing two hydrogen generation technologies, it is important to compare the process efficiency with the product hydrogen at equivalent temperature, pressure, and purity. For low temperature electrolysis, the primary impurity is water vapor which is typically managed through a drying process outside of the cell stack. The overall system efficiency can be described as follows, where η_{HHV} is the cell stack efficiency, $\eta_{P/S}$ is the electrical power conversion efficiency, and ξ is the ratio of auxiliary power (pumps, dryers, controls, valves, etc.) to stack power.

$$\eta_{overall} = \eta_{HHV} \cdot \frac{\eta_{P/S}}{1 + \xi}$$

f. Health & Safety Warning

Hydrogen is a flammable gas. It is combustible at levels of 4-75% volume in air. Hydrogen should only be produced in a well-ventilated area, and calculations should be performed to determine the maximum possible flow rate vs. the air flow in the area. Hydrogen can also embrittle metals over time, and materials of construction should be selected and inspected based on exposure.

4. Reference Section

M.J. Moran, H.N. Shapiro, *Fundamentals of Engineering Thermodynamics* (Wiley, ed. 3, 1996).