Thermodynamics of high-temperature, high-pressure water electrolysis

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HIGHLIGHTS

- We present electrochemical potentials for H_2O electrolysis up to 10^3 K and 10^2 MPa.
- Using advanced property models, errors of common ideal assumptions are quantified.
- Energy analyses study pressurized electrolysis versus product gas compression.

ARTICLE INFO

ABSTRACT

We report on a thermodynamic analysis for water electrolysis from normal conditions ($P = 0.1$ MPa, $T = 298$ K) up to heretofore unaddressed temperatures of 1000 K and pressures of 100 MPa. Thermoneutral and reversible potentials are determined using equations-of-state published by the International Association for the Properties of Water and Steam and the National Institute of Standards and Technology. The need for using accurate property models at these elevated temperatures and pressures is exemplified by contrasting results with those obtained via ideal assumptions. The utility of our results is demonstrated by their application in an analysis comparing pressurized electrolysis versus mechanical gas compression. Within the limits of our analysis, pressurized electrolysis demonstrates lower energy requirements albeit with electrical work composing a greater proportion of the total energy input.

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1. Introduction

Hydrogen is expected to play a critical role in future energy systems, by complementing or replacing fossil fuels in numerous applications [1,2]. Beyond its application in electrochemical and combustion systems as a zero-emissions fuel, hydrogen also serves as a feedstock in many industrial chemical processes (e.g., the Fischer-Tropsch processes for liquid hydrocarbon synthesis.) Currently, the largest portion of global hydrogen production involves the reformation of fossil fuels (mostly natural gas). Among the alternative, clean, hydrogen pathways is water electrolysis powered by renewable or other carbon-free sources.

We report on a thermodynamic analysis for water electrolysis from normal conditions ($p = 0.1$ MPa, $T = 298$ K) up to 1000 K and 100 MPa. The reversible and thermoneutral cell potentials as functions of temperature and pressure shall be described, and their

utility demonstrated via energy analyses of archetype systems featuring competing pressurization strategies.

Operation outside normal conditions is foreseen to be advantageous in terms of total energy consumption and energy utilization. Elevated temperature decreases the reversible work required to perform electrolysis, making cogeneration in thermal power plants viable [3]. Elevated pressure eliminates the need to compress product gases, at the expense of requiring a pressurized feedwater input. Hence, for an electrolysis plant, the lower energy required for pressurizing the denser water may improve overall efficiency. Additionally are possible reductions in electrochemical overpotentials; improved reaction kinetics, and enhanced mass transport performance especially in the supercritical phase. These overpotentials are however beyond the scope of this work.

Contemporary systems for hydrogen production via electrolysis can be classified, like their fuel cell counterparts, according to the ionic conductor type and the temperature of operation. Proton-exchange membrane electrolysis cells (PEMECs) operate between 70 and 100 °C, alkali cells 80–90 °C, and solid-oxide electrolysis cells (SOECs) at higher temperatures (600–1200 °C) [4–6]; all of which have operating pressures near atmospheric. Experimental

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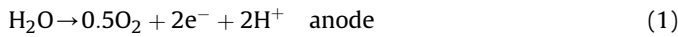 *E-mail address:* walter.merida@ubc.ca (W. Mérida).

efforts have explored the performance outside these conventional envelopes. For example: steam temperatures in proton-exchange membrane (PEM) systems using alternative membranes [7]; and pressurized PEMEC and SOEC systems, having achieved pressures of 7 MPa and 1 MPa respectively [5,6]. Alkaline systems, approaching [10] and in one case exceeding supercritical water conditions [11] have been reported.

Theoretical treatments that are complementary to experimental efforts are available. In an attempt to remedy perceived inaccuracies in the literature of the time, Leroy et al. calculated theoretical potentials for alkaline electrolysis in the ranges of 25−250 °C and 1−100 atm [12]. The expressions for enthalpies considered real gases, but ideal mixtures; whereas expressions for Gibbs free energy (and thus reversible potential) treated all species as ideal. The implications of different systems level operating strategies were not addressed. Onda et al. calculated theoretical potentials for (non-specific) electrolysis in the ranges of 25−250 °C and 1−700 atm [13]; applying these to high-pressure electrolysis systems analysis. Their work followed the expressions developed by Leroy, though with a different source for reference pressure properties as a function of temperature.

In the present study we address current challenges and knowledge gaps of the literature by: expanding the parameter ranges considered, incorporating advanced property models, demonstrating the error when inappropriate models are implemented, and analysing electrolysis configurations operating at the extremes of the ranges.

2. Method

The treatment assumes a reversibly operated electrolysis cell (i.e. without overpotentials); where the inlet stream is pure water of a single phase at prescribed pressure and temperature. The two independent outlet streams are pure hydrogen and oxygen at the same pressure and temperature. This is shown schematically in Fig. 1. The full and half-cell reactions for an (acid electrolyte) electrolysis cell are:

$$H_2O \rightarrow 0.5O_2 + 2e^- + 2H^+ \quad \text{anode} \tag{1}$$

$$2H^+ + 2e^- \rightarrow H_2 \quad \text{cathode} \tag{2}$$

$$H_2O \rightarrow H_2 + 0.5O_2 \quad \text{cell} \tag{3}$$

The net energy input (work & heat) required is given by the 1st law of thermodynamics. Neglecting potential, kinetic and other terms, it may be expressed for a control volume (CV) encompassing the cell operating at steady-state:

$$\frac{dE_{cv}}{dt} = 0 = \dot{Q} - \dot{W} + \dot{n}_{H_2O}\tilde{h}_{(H_2O|p,T)} - \dot{n}_{H_2}\tilde{h}_{(H_2|p,T)} - \dot{n}_{O_2}\tilde{h}_{(O_2|p,T)} \tag{4}$$
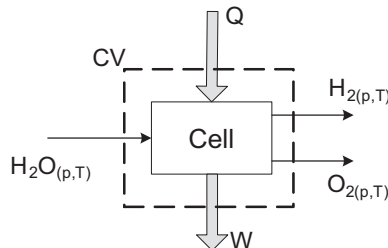

Fig. 1. System schematic.

where $\tilde{h}_{i|p,T}$ denotes molar enthalpy at temperature T and pressure p for species i. Rearranging and scaling terms per coulomb of charge transferred yields:

$$E_{th} = \frac{\dot{W} - \dot{Q}}{\dot{n}_{H_2}nF} = \frac{\tilde{h}_{(H_2O|p,T)} - \tilde{h}_{(H_2|p,T)} - 0.5\tilde{h}_{(O_2|p,T)}}{nF} \tag{5}$$

where E_{th} is the thermoneutral cell potential.

The reversible work input required is obtained by substituting the 2nd law of thermodynamics for the $\dot{Q}$ term of Eq. (4). What follows is an expression involving the Gibbs free energies of the species:

$$\dot{W} = \dot{n}_{H_2O}\left(\tilde{h}_{(H_2O|p,T)} - T\tilde{s}_{(H_2O|p,T)}\right) - \dot{n}_{H_2}\left(\tilde{h}_{(H_2|p,T)} - T\tilde{s}_{(H_2|p,T)}\right)$$
$$- \dot{n}_{O_2}\left(\tilde{h}_{(O_2|p,T)} - T\tilde{s}_{(O_2|p,T)}\right) \tag{6}$$

Rewriting the equation per coulomb of charge transferred yields the reversible cell potential.

$$E_{rev,cell} = \frac{\dot{W}}{\dot{n}_{H_2}nF} = \frac{\tilde{g}_{(H_2O|p,T)} - \tilde{g}_{(H_2|p,T)} - 0.5\tilde{g}_{(O_2|p,T)}}{nF} \tag{7}$$

The quality of a (thermo analysis) model is contingent on the accuracy of supporting data. This work makes use of the most recent equations-of-state (EOS) for thermodynamic properties recognized by: the International Association for the Properties of Water and Steam (IAPWS), the National Institute of Standards and Technology (NIST), and the International Council for Science : Committee on Data for Science and Technology (CODATA). More specifically, the following sources are used:

- For water, this analysis uses the IAPWS 1995 release on the properties of ordinary water, as implemented in the WATER95 MATLAB library [14,15]. IAPWS-95 describes water over the ranges of the melting pressure curve to 1273 K at 1000 MPa, though this may be extended to 100 GPa and 5000 K.
- For (normal) hydrogen, this analysis uses an expression developed by Leachman et al., valid up to 1000 K and 2000 MPa [16].
- For oxygen, this analysis uses an expression developed by Schmidt and Wagner [17]. Originally conceived for an upper limit of 300 K and 818 bar, it may be extrapolated with accuracy to 1000 K and 100 MPa [18].
- For translation of the aforementioned data to a consistent reference frame, this analysis uses standard-state enthalpy of formation and entropy from CODATA Key Values for Thermodynamics [19].

The aforementioned equations-of-state describe succinctly the thermodynamic properties of their respective fluids via two-part expressions for non-dimensional Helmholtz free energy as a function of reduced density and reduced inverse temperature (Eq. (8)).

$$\phi(\delta, \tau) = \phi^0(\delta, \tau) + \phi^r(\delta, \tau) \quad \text{where}: \phi = \frac{a}{RT} \quad \delta = \frac{\rho}{\rho_c} \quad \tau = \frac{T_c}{T} \tag{8}$$

Such description is advantageous as it does not require ancillary equations (e.g.: is not susceptible to errors from multiple equation incongruities). Appropriate partial derivatives of the ideal and residual Helmholtz free energy components yield the necessary parameters (Eqs. (9)–(11)).