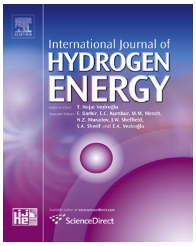
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 39 (2014) 13063–13078

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Influence of operation parameters in the modeling of alkaline water electrolyzers for hydrogen production

*Ernesto Amores**, *Jesús Rodríguez, Christian Carreras*

Research Department, Centro Nacional del Hidrógeno, Prolongación Fernando El Santo s/n, 13500 Puertollano, Ciudad Real, Spain

ARTICLE INFO

Article history:
Received 25 February 2014
Received in revised form
25 June 2014
Accepted 1 July 2014
Available online 23 July 2014

Keywords:
Alkaline water electrolysis
Hydrogen
Modeling
Renewable energy

ABSTRACT

In order to improve the production of environmental friendly hydrogen, new advanced alkaline electrolyzers must be designed to optimize their combination with renewable energies. In pursuing this goal, modeling of alkaline electrolyzers becomes a powerful design tool. In this paper is presented a mathematical model that describes the behavior of an alkaline electrolysis cell. Unlike most of the existing models in literature, the proposed model simulates the influence of both electrode/diaphragm distance and electrolyte concentration in regular operation. The role of these aspects is crucial when designing alkaline electrolyzers since the process efficiency is found to be very sensitive to them. The computations done with the model presented here were validated with in situ experimental data, reporting a great accuracy: the maximum error was around 1% from all polarization curves studied. Combination with renewable energies was also studied by introducing a solar PV profile and the error reported never exceeds 3%. The influence of the considered variables (temperature, electrode/diaphragm distance and electrolyte concentration) was quantified using sensitivity analysis.

Introduction

The current fossil fuel-based energy and transportation system is not sustainable due to [1–3]:

- Rapidly growing energy demand in the near future due to population growth and the progressive industrialization of developing nations.
- Negative environmental impact of fossil fuel combustion (climate change due to the greenhouse effect of anthropogenic CO_2).
- Excessive economic dependence on oil producing countries.

Renewable energy sources can solve some of these problems, but their inherent dependence on weather conditions causes them to be intermittent. In this context, hydrogen offers a promising solution since it can be made from electricity generated by renewable energy sources and then stored and/or transported. In addition, it could provide a sustainable fuel for transportation, for portable applications, and for power supplies to electronic devices [1,4,5]. Moreover, hydrogen production could also be an attractive option for remote areas

---

* *Corresponding author*. Tel.: +34 926 420 682.
E-mail addresses: ernesto.amores@cnh2.es (E. Amores), jesus.rodriguez@cnh2.es (J. Rodríguez).

http://dx.doi.org/10.1016/j.ijhydene.2014.07.001

Abbreviations, nomenclature and units

Acronyms

DC	direct current
HYSOLAR	hydrogen solar
PIV	particle image velocimetry
PV	photovoltaic
RE-H_2	renewable energy combination-Hydrogen
RE	renewable energy
SCADA	supervisory control and data acquisition
SIMELINT	simulation of electrolyzers in intermittent operation
TRNSYS	transient system simulation software

Symbols

a	activity
A	electrodes area, m^2
C	electrolyte concentration, M
d	electrode/diaphragm distance, mm
F	Faraday constant, 96,485C mol^{-1}
H	electrode height, m
i	current density, A m^{-2}
I	current, A
k	specific conductivity, S cm^{-1}
p	parameter related to ohmic resistance (specific conductivity), Ω m^2
P	pressure, bar
q	parameter related to ohmic resistance (electrode/diaphragm distance), Ω m^2
r	parameter related to ohmic resistance (electrolyte), Ω m^2
R	universal gas constant, 8.314 J K^{-1} mol^{-1}
s	coefficient for overvoltage on electrodes, V
t	coefficient for overvoltage on electrodes, A^{-1} m^2
T	temperature, °C
u	bubble rising velocity, m s^{-1}
U	voltage, V
z	number of electrons transferred per reaction

Subscripts

cell	electrolysis cell
$e–e$	electrode/electrode
$e–d$	electrode/diaphragm
exp	experimental
irrev	irreversibilities
opt	optimal
rev	reversible
sim	simulation

such as islands without access to the primary grid, and an economic alternative in countries with a large renewable resource base but lacking fossil resources [1].

Hydrogen can be obtained by different ways, but the “renewable energy- hydrogen” combination (RE-H_2) by electrolysis is probably one of the most environmental friendly strategies. For this reason, in the past decades, great attention on interaction RE-H_2 was paid by energy companies, in order to position themselves in the future markets of distributed power generation and alternative fuels [6]. Among the different electrolysis technologies, alkaline water electrolysis is optimal for large scale hydrogen production because it is an economic and mature technology [7].

Nonetheless, as wind and solar energy are highly dependent on weather conditions, fluctuations of power supplied to an electrolyzer could cause different problems such as: generation of explosive mixtures, corrosion of materials, pressure drops and decreased efficiency, among many others. In order to avoid these problems, electrolyzer modeling provides a useful design and optimization tool to foster the properly design of alkaline electrolyzers powered by renewable energies.

Most of the relevant models for electrolyzers available in bibliography are related to solar-hydrogen demonstrations [6]. One of the most detailed models is probably the SIMELINT-program, which was validated against experimental data and it predicted the electrolyzer behavior accurately in the HYSOLAR project [8]. Another outstanding solar-hydrogen model was developed in the Fraunhofer Institute by Griesshaber and Sick [9], and later validated by Mørner [10] in the frame of Self-Sufficient Solar House (SSSH) project, as a subroutine of simulation program TRNSYS [11]. Afterwards, Ulleberg [6] reported in 2003 a dynamic 0-D model for an alkaline electrolyzer, taking as reference the work of Griesshaber and Sick [9]. The model is based on a combination of fundamental thermodynamics, heat transfer theory and empirical relationships, and it is able to simulate the dynamic behavior of an alkaline electrolyzer. This model has taken great attention and it has been frequently used for dynamic simulation of RE-H_2 systems because of its accuracy and adaptability to different electrolyzers. Diéguez et al. [12] studied the thermal performance of a commercial alkaline water electrolyzer (HySTAT from Hydrogenics) under different operating conditions using an adaptation of the electrochemical model proposed by Ulleberg. Valenciaga and Evangelista [13] presented a control scheme to manage the operation of an autonomous wind based hydrogen production system with the same model. Đukić and Firak [14] developed and tested an alkaline electrolyzer supplied with a PV panel including a mathematical model to improve the system according to Ulleberg's model. Carapellucci and Giordano [15] carried out a simulation tool for evaluating energy and economic performance of renewable islands, including various technologies for electricity generation, integrated with a hydrogen storage system using the same $I–U$ model for the alkaline electrolyzer. Mori et al. [16] conducted an experimental investigation of a commercial alkaline water electrolyzer for hydrogen production to balance decentralized electricity production from renewable energies and for the evaluation of different operating pressures on the performance of the electrolyzer, using this empirical $I–U$ model. Khalilnejad and Riahy [17] used Ulleberg's model for the design and modeling of an advanced alkaline electrolyzer in combination with a hybrid wind-photovoltaic system, in order to maximize the production of hydrogen.

However, although electrochemical and thermodynamic effects are key considerations when designing an electrolyzer, there are other parameters equally important such as the electrolyte concentration or the cell architecture. These