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Electrochemical analysis of a photoelectrochemical chloralkali reactor

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ABSTRACT

In the present study, the electrochemical model for a newly designed photo electrochemical hydrogen production reactor is discussed. The reactor integrates the photochemical hydrogen production with an electrochemical chloralkali process. To neutralize the hydroxyl ions into the chloralkali process, the ideal minimum required potential is 2.18 V. However, there are losses in the solution, membranes and electrodes. These losses should be calculated to find the exact voltage requirement of the photoelectrochemical hydrogen production reactor. An electrochemical model is developed to calculate these losses in the reactor. Effect of brine concentration, electrolyte concentration, distance between the electrodes, current density and temperature are evaluated. The results show that a minimum voltage is required when the distance between the electrodes becomes a minimum at the highest possible temperature, lowest current density and at highest concentrations of brine and electrolyte. Furthermore, they indicate that brine and electrolyte concentrations do not have significant effect on required voltage.

1. Introduction

Hydrogen is a clean and green energy carrier with a high heat of combustion (app. 286 kJ/mol). Among different methods, electrolysis of water is a standard process of producing hydrogen. The potential required to produce hydrogen from water depends on the nature of reaction, decomposition voltage and ohmic losses in different components of the reactor. The decomposition voltage and ohmic losses depend on concentrations of solutions and processing parameters. Electrochemical modeling is used to find out the desired potential of electrochemical cell.

Numerous researchers have studied different areas of electrochemical modeling for different processes. For example Tailor et al. [1] studied evolution of electrochemical finishing processes through cross innovations and modeling. Mandin et al. [2] discussed electrochemical engineering modeling of the electrodes kinetic properties during two-phase sustainable electrolysis. Volgin et al. [3] presented mathematical modeling of three-dimensional electrochemical forming of complicated surfaces. Colombo et al. [4] explained ion transport in tumors under electrochemical treatment: in vivo, in vitro and in silicone modeling. Gheem et al. [5] examined a theoretical approach for modeling electrochemical impedance measurements using a rational function in $j\omega$. Elleuch et al. [6] described analytical modeling of electrochemical mechanisms in CO_2 and CO/CO_2 producing direct carbon fuel cell. Jiawen et al. [7] studied modeling of NC-electrochemical contour evolution machining using a rotary tool-cathode. Scott [8] described modeling for different surface electrochemical reactions.

Andersson et al. [9] performed SOFC modeling considering electrochemical reactions at the active three phase boundaries. Dees et al. [10] examined electrochemical modeling of lithium polymer batteries. Georgiadou [11] studied modeling of current density distribution in different electrochemical systems. Park et al. [12] conducted an analysis of different chemical, electrochemical reactions and thermo-fluid flow in methane-feed internal reforming SOFCS. Chikhi et al. [13] described current distribution in a chloralkali membrane cell. They performed an experimental study and modeling of the membrane cell. Jalali et al. [14] studied the effects of process conditions on cell voltage, current efficiency and voltage balance of a chlor-alkali membrane cell. Chandran and Chin [15] performed a reactor analysis for membrane cell. They also studied electrochemical modeling of the two chamber membrane cell.

Dong et al. [16] discussed electrochemical performance of porous Ni_3Al electrodes for hydrogen evolution reaction. Savari et al. [17] studied electrolysis of sodium chloride using composite poly(styrene-co-divinylbenzene) cation exchange membranes. Bennett et al. [18] developed a model of charge transport and electromechanical transduction in ionic liquid-swollen nafion membranes. Nagarale et al. [19] reviewed recent developments

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Nomenclature

E	decomposition voltage (V)
F	Faraday constant (sA/mol).
i	current density (kA/m^2)
K	electrical conductivity (1/ohm m)
l	distance (m)
Mo	molality
P	partial pressure (kPa)
R	universal gas constant (J K^{-1} mol^{-1})
T	temperature (°C)
V	voltage (V)

Superscript and subscript

A	anode
AEM	anion exchange membrane
Brine	brine solution
CEM	cation exchange membrane
C	cathode
Cl_2	chlorine
H_2	hydrogen
NaOH	sodium hydroxide
H_2O	water
NaCl	sodium chloride
Sol	solution
o	exchange

Greek letters

γ	activity coefficient
σ	membrane thickness

on ion-exchange membranes and electro-membrane processes. Yin et al. [20] studied electricity production and electrochemical impedance modeling of microbial fuel cells under static magnetic field. Mounir et al. [21] discussed thermo-fluid and electrochemical modeling of a multi-bundle IP-SOFC technology for second generation hybrid application. Qu et al. [22] performed three-dimensional thermo-fluid and electrochemical modeling of anode-supported planar solid oxide fuel cell. Xue et al. [23] performed dynamic modeling of single tubular SOFC combining heat/mass transfer and electrochemical reaction effects. Sahraoui et al. [24] presented two-dimensional modeling of electrochemical and transport phenomena in the porous structures of a PEMFC.

Pirkandi et al. [25] carried out an electrochemical and thermodynamic modeling of a CHP system using tubular solid oxide fuel cell. Ni et al. [26] studied mathematical modeling of the coupled transport and electrochemical reactions in a solid oxide steam electrolyzer for hydrogen production. Wang et al. [27] performed modeling of a microfluidic electrochemical cell for CO_2 utilization and fuel production. Ho et al. [28] carried out modeling of transport, chemical and electrochemical phenomena in a cathode-supported SOFC. Ledovskikh et al. [29] studied electrochemical modeling of hydrogen storage in hydride-forming electrodes. Brunini et al. [30] performed modeling of the hydrodynamic and electrochemical efficiency of semi-solid flow batteries. Doche et al. [31] examined direct numerical simulations of electrochemical reactions in turbulent flow. Datta et al. [32] discussed several different applications of electrochemical micro fabrication. Fonocho et al. [33] carried out a study of the electrochemical hydrogenation of o-xylene in a PEM hydrogenation reactor. Salmi et al. [34] performed modeling of multistep electrochemical reactions in molten salt electro-winning of refractory metals.

The objective of the present study is to perform the electrochemical modeling and analysis of a newly designed photoelectrochemical hydrogen production chloralkali reactor. Electrochemical analysis is used to find the overall potential in the chloralkali cell. The effects of different parameters on the cell voltage are determined. The parameters include current density (kA/m^2), distance between electrodes (mm), cell temperature (°C), brine concentration levels (g/425 mL), and electrolyte concentration (g/425 mL) in the catholyte compartment. For the purpose of parametric study, $l_1 = l_2 = l_3 =$ distance is used in this simulation as a key parameter.

2. Hydrogen production and neutralization of OH^- ions

During the hydrogen production process from water, water is reduced into hydrogen and hydroxyl ions given as follow.

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{1}$$

The hydroxyl ions can be oxidized into different processes. If these hydroxyl ions are oxidized into oxygen and water, then the reaction is given as follow

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \tag{2}$$

The minimum required potential for reaction (1) is 0.83 V and the minimum oxidization potential for reaction (2) is 0.4 V. Therefore the net required potential to break water into hydrogen and oxygen is 1.23 V. Similarly, these hydroxyl ions from reaction (1) can also be oxidized into a chloralkali process. In chloralkali process, chlorine is produced at the anode

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{3}$$

The minimum required potential for reaction (3) is 1.35 V. The overall chloralkali reaction becomes

$$2H_2O + 2NaCl \rightarrow Cl_2 + H_2 + NaOH \tag{4}$$

where the net minimum required potential for reaction (4) is 2.18 V. However there are losses associated with the process. These losses increase the required potential for the redox reaction of water or salt water. These losses should be calculated to find the required potential for the reaction to occur. This requires electrochemical modeling of the system.

On the other hand, most of the research on photochemical hydrogen production from water which is presented in literature does not discuss the extraction and neutralization of hydroxyl ions. Also it has been observed in previous literature that the rate of photochemical (i.e. also referred as photocatalytic) hydrogen production decreases over time due to the increasing concentration of hydroxyl ions in the hydrogen production solution. These hydroxyl ions should be extracted from the photocatalytic system and should be neutralized in either of the above mentioned process. A new photoelectrochemical reactor has been designed. Fig. 1 shows the schematic of a newly designed photoelectrochemical chloralkali process reactor. It integrates the photochemical hydrogen production process with electrochemical chloralkali process for continuous hydrogen production (i.e. neutralize the hydroxyl ions from the photochemical hydrogen production in a chloralkali process). It consists of three compartments, namely: hydrogen production, sodium hydroxide production and chlorine production. The sodium ions travel through the cation exchange membrane and combine with hydroxyl ions. Combination of sodium and hydroxyl ions results in formation of sodium hydroxide. Hydrogen is produced by means of a photocatalytic and electrochemical process while chlorine is produced by only an electrochemical process.

Since photochemical hydrogen production (i.e., so-called: photocatalytic hydrogen production) uses only a portion of the solar spectrum for reaction (1), from an energy efficiency and cost perspective it is important to recover the unused portion of the solar