Numerical investigations on ethanol electrolysis for production of pure hydrogen from renewable sources

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HIGHLIGHTS

- Ethanol electrolysis process to produce hydrogen was investigated numerically.
- The model considers the transport phenomena and electrochemical reactions in the cell.
- Reasonable agreement was found between the experimental data and numerical results.
- Optimal operating potential for the electrolytic cell is proposed to be 0.94 V.

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ABSTRACT

Hydrogen and fuel cells have the potential to play a significant role in the energy-mix network and providing a more sustainable future. Hydrogen is mainly produced from steam-reforming of natural gas and water electrolysis. However, it is suspected that the production of hydrogen through the electrolysis of ethanol is more energy efficient and more environmentally friendly. In this study, to gain a good insight of ethanol electrolysis process, we have investigated the ethanol electrolysis in a polymer electrolyte membrane (PEM) reactor numerically. A two-dimensional, isothermal, and single phase ethanol electrolyzer numerical model, taking into account the transport phenomena and electrochemical reactions, has been developed for such purpose. Besides, a systematic parametric study is carried out to elucidate the effect of operating temperature, flow rate and the thickness of the membrane on the performance of the electrolytic cell. A reasonable agreement is found between the numerical data and the experimental results available in the literature indicating the predictive capability of the model.

1. Introduction

The significant growth of demand for clean energy has motivated scientists in the field of energy science to pursue alternative methods for power generation [1–7]. Hydrogen has been considered as a promising energy carrier as it possesses substantial energy density. Moreover, hydrogen is environmentally friendly and certainly can contribute to a clean and sustainable environment [8–11]. There are several ways to produce hydrogen, preferably from renewable energy sources. Currently, steam reforming of hydrocarbons or alcohols is widely used for the mass production of hydrogen [12–17]. Nevertheless, there is a desire to develop renewable hydrogen production technologies. Hence, electrolysis

has been explored as a potential method to produce hydrogen because the energy input to the electrolysis process can be derived from renewable energy sources [12]. In recent years, various studies have been conducted on the electrolysis of water as a source of pure hydrogen production [18–23]. However, the amount of energy required for the water electrolysis is significantly higher. The theoretical cell potential for hydrogen evolution through water electrolysis process is 1.229 V. Therefore, the electrolysis of alternative liquids like alcohols has been explored to reduce the amount of energy needed [24,25]. Moreover, the electrolysis of alcohols can be considered environmentally friendly if bio-alcohol is used as the fuel [11,26]. There are several studies done on hydrogen generation through methanol electrolysis [27–29]. However, methanol is very toxic in nature. Among all the other alcohols, ethanol is a suitable candidate for transportation and stationary applications, due to its high energy density and non-toxicity compared with methanol. The energy densities of ethanol and methanol (LHV) are 29 MJ/kg and 19.7 MJ/kg, respectively.

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Nomenclature

D	diffusivity ($m^2\ s^{-1}$)
E	standard electrode potential (V)
F	Faraday constant (96,487 C mol^{-1})
i	current density (A cm^{-2})
LHV	low heating value
M	molar mass (kg mol^{-1})
n	molar flux (mol s^{-1})
P	pressure (Pa)
Q	electrical power (J s^{-1})
T	temperature (K)
u	velocity vector (m s^{-1})
V	specific rate of generation/consumption

Greek characters

σ	conductivity (S m^{-1})
φ	potential (V)
ε	porosity
η	over-potential (V)

λ	membrane water content
μ	viscosity (kg m^{-1} s^{-1})
ρ	density (kg m^{-3})
ω	weight fraction
γ	efficiency

Subscripts and superscripts

a	anode
act	activation
cath	cathode
E	ethanol
eff	effective
m	membrane
p	parasitic
s	gas distribution electrode

Moreover, huge potential for easy production of ethanol through fermentation of sugar-containing materials [30] inspired us to choose ethanol electrolysis.

The two half-cell reactions of the electrochemical reforming of ethanol are presented in Eq. (1).

a. $CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$

b. $2H^+ + 2e^- \rightarrow H_2$ (1)
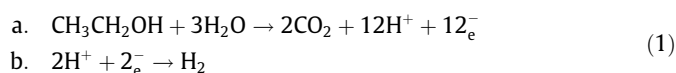
with ΔH = +348 kJ/mole ethanol and ΔG = +96.9 kJ/mole ethanol. The number of electrons transferred during the reaction is 12. Hence, the theoretical cell voltage for ethanol electrolysis, obtained from the Gibbs free energy equation $E_{EtOH} = \Delta G/n$, has become 0.08 V. This leads to less energy requirement compared to water electrolysis resulting in higher energy efficiency.

All the studies performed in the past on electrolysis of ethanol for hydrogen production have been purely experimental in nature [31]. To-date, there is no mathematical modeling study on ethanol electrolysis found in the literature. This is, perhaps, the first computational fluid dynamics study on the ethanol electrolysis based on PEM electrolytic cell. This study formulates an isothermal, two-dimensional and single phase model of the electrolysis of ethanol with detailed process of flow of the water–ethanol solution, electrochemical reactions and species transport within the electrolytic cell. Furthermore, the effect of the feedstock flow rate and operating voltage on the species composition and cell performance is studied and discussed.

2. Theory

The two-dimensional schematic of a PEM ethanol electrolyzer and the computational domain are shown in Fig. 1. The electrolyzer cell includes anode and cathode flow channels of straight type, anode and cathode electrodes and an electrolyte, which is sandwiched by the electrodes. Pt/C is considered to be the electrocatalysts used. Water–ethanol mixture is supplied to the anode side and hydrogen is generated in the cathode compartment. Ethanol molecules are oxidized in the presence of water molecules into carbon dioxide and protons as presented in Eq. (1). Twelve electrons are involved in this electrochemical reaction. The electrons react with protons transported through the membrane and generate hydrogen at the cathode catalyst layer. The generated hydrogen molecules diffuse out of the cathode electrode to the cathode flow channel. CO_2 molecules produced at the anode side are transported out by the residual ethanol solution stream. The crossover of the ethanol molecules from the anode side to the cathode may also take place. Ethanol molecules transported to the cathode side are oxidized at the cathode. The current produced due to the oxidation of ethanol at the cathode side is considered as the parasitic current (i_p). When this occurs, there is a mixed potential at the cathode due to concurrent oxidation and reduction processes.

Because the flows in the channels of a PEM electrolyzer have small Reynolds number, they are assumed to be in laminar regime. In addition, the steady state condition is considered for the computational fluid dynamics model. The charge balance is solved in the electrodes and the membrane with Eqs. (2) and (3), respectively.

$$-\nabla \cdot \left(\sigma_{eff}^s \nabla \varphi_s \right) = 0 \tag{2}$$

$$-\nabla \cdot (\sigma_m \nabla \varphi_m) = 0 \tag{3}$$

where σ_{eff}^s, φ_s, σ_m, and φ_m are the electric conductivity and the potential of the porous electrodes and the membrane, respectively. The membrane conductivity is a function of the water content of the membrane λ, i.e., the concentration ratio of water to sulfonic acid group in the membrane. The following experimental expression for the conductivity of Nafion membrane has been presented by Springer et al. [32].

$$\sigma_{30} = 0.5139\lambda - 0.326, \quad for\ \lambda > 1 \tag{4}$$

where σ_{30} and λ are the membrane conductivity in S m^{-1} (measured at 30 °C) and water content of the membrane, respectively. The conductivity at any given operating temperature can be calculated using Eq. (5).

$$\sigma_m = \exp\left[1268\left(\frac{1}{303} - \frac{1}{T} \right) \right] \sigma_{30} \tag{5}$$

The flow in the porous media of the gas diffusion layers of the PEM fuel cell is modeled by Darcy's law (Eq. (6)), where the pressure gradient is the driving force.

$$\nabla p = -\frac{\mu}{\kappa}u + \frac{\mu}{\varepsilon}\nabla^2 u \tag{6}$$

where u, k_p, μ, ε, and p are the velocity vector, permeability of the porous media, viscosity of the fluid, porosity and pressure, respectively. The governing equations and the boundary conditions are summarized in Fig. 1b. The boundary condition for the mass and