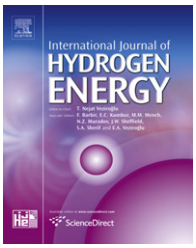
Available at www.sciencedirect.com

ScienceDirect

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



Comparison between direct small molecular weight alcohols fuel cells' and hydrogen fuel cell's parameters at low and high temperature. Thermodynamic study

*M. Nacef, A.M. Affoune**

Laboratoire d'Analyses Industrielles et Génie des Matériaux, Département de Génie des Procédés, Université 8 mai 1945, BP 401, Guelma, Algeria

ARTICLE INFO

Article history:
Received 15 April 2010
Received in revised form
21 June 2010
Accepted 22 June 2010
Available online 7 August 2010

Keywords:
Fuel cells
Alcohols
Reversible efficiency
Electromotive force
Specific energy
Energy density

ABSTRACT

In this paper, direct alcohol fuel cells' thermodynamics parameters were calculated by means of analytical formulas using thermodynamic data. The effect of temperature on reversible efficiency, electromotive force and specific energy for fuel cells supplied with alcohols having from one to five carbons was studied in the range between 298.15 and 1300 K.

All parameters were also compared with those of hydrogen fuel cell. It was found that reversible efficiency, electromotive force and specific energy are a function of the amount of carbon atoms in the fuel and a function of temperature. In addition, alcohol's structure influences fuel cells' parameters too.

We have found that there is a competition between hydrogen, ethanol and methanol at standard conditions, while methanol, ethanol, propanol isomers, 2-methylpropan-1-ol and butan-2-ol, as classified, appear more indicated than hydrogen at more elevated temperature.

Therefore, the approach presented here can be considered as sufficient enough for a primary choice of an alcohol that could be used in fuel cells in the future.

1. Introduction

Fuel cells have been widely recognized as one of the cleanest and most efficient alternatives for generating electricity with near zero pollutant emission, high efficiency, low noise, and extensive research is ongoing to improve the reliability and reduce the cost of these electrochemical devices. Most fuel cell types require hydrogen as fuel [1], but hydrogen is more expensive with difficulties of storing it without mentioning transport and distribution compared to traditional hydrocarbon fuels. Direct alcohol fuel cells (DAFCs) have also attracted considerable interest in their application to alternative power sources for automobile and portable consumer electronics [2–5].

DAFCs have several advantages such as their use of liquid fuels, simple construction without a reformer, low weight and low cost. Furthermore, alcohols combustion reaction provides much more electrons than that of hydrogen combustion reaction. Methanol is a promising fuel for DAFCs, but other low-molecular weight alcohols such as ethanol and propan-1-ol are also candidates. Nevertheless, DAFCs have suffered slow kinetics of alcohol electrooxidation on electrode surfaces in spite of great efforts have been made toward the development of catalyst materials [6–9].

* *Corresponding author*. Tel.: + 213 37 21 58 52; fax: +213 37 20 72 68.
E-mail addresses: nacef2010@yahoo.fr (M. Nacef), affoune2@yahoo.fr (A.M. Affoune).
0360-3199/$ – see front matter
doi:10.1016/j.ijhydene.2010.06.075

Nomenclature

Cpi	specific heat for species i at constant pressure, J mol^{-1} K^{-1}
d	fuel density, kg m^{-3}
emf	electromotive force at equilibrium, V
F	Faradays' constant, 96,485 C mol^{-1}
Lv_a	latent heat of vaporisation for alcohol, J mol^{-1}
Lv_w	latent heat of vaporisation for water, J mol^{-1}
M	molar weight, g mol^{-1}
n	number of carbons in alcohol
n_e	electrons number involved in the whole reaction of fuel cell
Q_{in}	heat supplied to the system, J
R	universal gas constant, J mol^{-1} K^{-1}
T	cell temperature, K
Teb_a	boiling temperature for alcohol, K
Teb_w	boiling temperature for water, K
T_h	higher temperature of supplied heat to engine, K
T_l	lower temperature of dumped heat from engine, K
W	fuel specific energy, kWh kg^{-1}
W_e	fuel energy density, kWh m^{-3}
W_{elec}	electrical work
W_{out}	work done by the system

Greek letters

ε	reversible efficiency of the cell
ξ	stoichiometric coefficient of reactants or products
ΔCp_r	specific heat change for the reaction, J mol^{-1} K^{-1}
ΔE	the difference in electric potential
$\Delta G°r$	standard free Gibbs energy change, kJ mol^{-1}
$\Delta H°_r$	standard enthalpy change, kJ mol^{-1}
$\Delta H°_{f\,(i)}$	standard enthalpy of formation for species i, kJ mol^{-1}
$\Delta S°r$	standard entropy change, J k^{-1} mol^{-1}
η_{anode}	anode polarization
$\eta_{cathode}$	cathode polarization

One way to improve fuel cells anodic as well as cathodic reactions is to operate at high temperature. This improvement could be achieved by three approaches:

i) Reducing the poisoning effect of carbon monoxide. While operating less than 120 °C only a little amount of CO, ca. 10 ppm poison the electrocatalyst [10]. Meanwhile, it has been demonstrated that CO coverage reduces with increasing temperature, becoming negligible above 140 °C, [10,11].
ii) The overall reactions kinetics increase while rising temperature, leading to fewer amounts of electrocatalysts, and so reducing fuel cell cost.
iii) Interlayer diffusion of reactants and products will increase with rising temperature, as a result of fuel state. In other words, gaseous fuels diffuse more effectively than liquid fuels.

Furthermore, elevating fuel cell temperature has other benefits, like better evacuation of cell temperature because of the difference between the inside cell and room temperature. In addition, heat could be used in cogeneration system for house heating as an example.

By using current proton conducting membrane in today's technologies, fuel cells operating at high temperature are not feasible.

First, they are degradated at 110–130 °C as a result of the glass transition temperature [12]. Second, these membranes conduction is depending on the hydration. In fact, membrane water leaching becomes critical above 120 °C [13,14]. Today, the design and preparation of PEMFCs' membranes suitable for higher temperature is one of the major challenges facing the fuel cell's research. Polybenzimidazole membranes are being developed and results exhibit good stability at higher temperatures [15,16]. Others [17–22], introduced composite membranes that can operate at higher temperature. In the same way, several attempts have suggested a new kind of membranes that can replace acid membranes, which are called water-free membranes [23,24].

The first aim of this work was to focus on PEMFCs, but the use of the general theory led us to extend calculations to more elevated temperature fuel cells' as oxide fuel cell that operate at 1000 °C. These fuel cells are fuelled mainly with hydrogen and they could be fed by alcohols too [25–27].

In this study, we try to show how elevating temperature influences fuel cells' parameters such as reversible efficiency, electromotive force and specific energy. Fuel cells concerned by the present work are those fed by hydrogen and light weight alcohols having from one to six carbons in their structure. A large number of works has studied the electro-oxidation of methanol and ethanol [28–37], more less has been done for propanol and butanol isomers, pentanol and also hexanol [38–43], but in the best of authors knowledge, there are no researches focused on theoretical study of fuel cells gathering such a number of fuels compared to hydrogen fuel cell. This work will lead future researches for using one of these alcohols.

2. Basic thermodynamics of fuel cells

Fuel cell is composed of two electrodes separated by an electrolyte (Fig. 1); the anode where fuel is fed and oxidized:

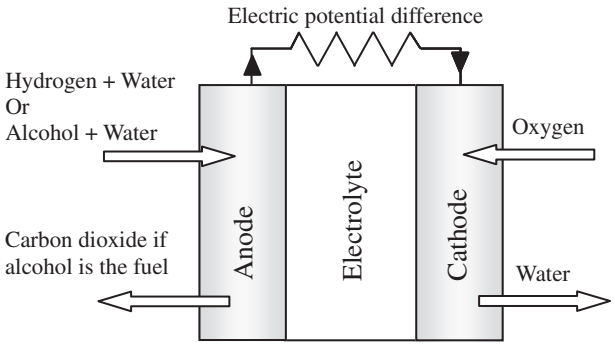


Fig. 1 – Schematic depiction of a fuel cell fed with hydrogen or alcohol.