Journal Food and Environment Safety of the Suceava University – FOOD ENGINEERING, Year IX, No1 - 2010

STUDIES REGARDING THE EFFICIENCY OF A DIRECT METHANOL FUEL CELL (DMFC)

Violeta VASILACHE

Stefan cel Mare University of Suceava, Faculty of Food Engineering. 13 th University Street, 720229, Romania,
E-mail adress: violetav@usv.ro

Abstract: *Combustion cells are devices which transform chemical energy into electric and thermal energy. There could be an acceptable solution to the problem of alternative sources of energy, for a lot of practical applications. DMFC combustion cell (DMFC – direct methanol fuel cell) uses methanol, instead of hydrogen, so it works safely. More, the storage of combustible does not represent a difficult problem, like the hydrogen storage presents. A reforming device is not necessary, because the cell itself transforms methanol into hydrogen protons, free electrons and CO_2. The absence of reforming device make this type of cell more adapted for automotive applications where the objective is to have a simple source of electric power. A polymeric membrane which could conduct protons is used as electrolyte. The technology DMFC (direct methanol fuel cell) is in fact a variant of PEMFC (polymer electrolyte membrane fuel cell) technology, which was developed having hydrogen as combustible. Using chemical reactions, the efficiency was calculated theoretically to find the possibilities of increasing it. Thermodynamic considerations were also used to complete the efficiency study. Finally, using scientific data, a calculus was performed.*

Keywords: *methanol fuel cell, material and energy balance, thermodynamic*

Introduction (actual state of research)

Surampidi and co. have studied the effect of temperature and of the methanol concentration through efficiency in a DMFC. The performances were measured at 30ºC, 60ºC and 90°C respectively, and the results prove an increase of performances with increasing the temperature. They worked with concentrations of 0,5, 2,0 and 4,0 M; higher voltage was obtained for 2,0 M concentration when the current density was higher too. Optimal concentration was between 0,5 and 2,0 M. *Jung and co*. studied the effect of working temperature for the range 60-120°C and of the methanol concentration for the range 0,5-4,0 M. The methanol flow on anode was 9 *ml/min* and the pure oxygen flow was 105 *sccm*. The results also confirmed the fact that performances of the cell are increasing with temperature and the optimal concentration was 2,5 M. *Nakagawa and Xiu* studied a cell in the temperatures range from 30ºC to 100°C and the effect of proportion of oxidant gas (air and pure oxygen respectively)[1,2,3,4].

Recent studies at *Los Alamos National Laboratory* (LANL) focalized on possible applications of DMFC as principal and auxiliary power source for vehicles and as a portable power source for the range 1-100 *W*. The conditions in exploitation force some restrictions, so working temperatures have not to be higher than 100°C and the consumption of precious metals has to be reduced at minimum. For portable power sources the temperature should not exceed 80°C, but the power demands are reduced, fact that imposes a decreasing of consumption of noble metals [5,6].

Theory, studies, results and discussion

Function of a DMFC is based on next phases:

Phase1. Those two gases, oxygen (air) and methanol, maintained in two separated tanks – oxygen on the cathode side and methanol on anode side, flow from tank to catalyzer.

Phase2. Methanol (CH_3OH) reacts with water forming carbon dioxide and hydrogen. At catalyzer side, hydrogen is decomposed into two atoms of H^+ (protons) and every atom yields its electron in this process[7,8].

Phase3. Protons pass through electrolyte (polymeric membrane capable to conduct protons) and displace to cathode.

Phase4. Electrons migrate from anode to cathode and generate an electric current (electric power).

Phase5. At contact with cathode, four electrons always recombine with an oxygen molecule.

Phase6. Just formed oxygen ions have a negative electric charge, and furthermore react with protons forming water.

The chemical reactions occurring are:

At anode side:

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad \text{(oxidation)} \qquad (1)$$

At cathode side:

$$3/2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \quad \text{(reduction)} \qquad (2)$$

Total reaction:

$$CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O \qquad (3)$$

The efficiency of a combustion cell can be measured by measuring the potential curve V(I). Generally the next relation should be taken into consideration:

$$V(I)=\varepsilon_0 - \eta_{act}(I) - \eta_{ohm}(I) - \eta_{conc}(I), \qquad (4)$$

where ε_0 is a constant term which represents the value of potential difference of the cell in open circuit ($I=0$); $\eta_{act}(I)$ is a logarithmic term (activation over-potential), which represents a lose connected with the activation energy for starting electrochemical reactions, important for lower values of the current density; $\eta_{ohm}(I)$ is a linear term, representing potential drop due to the ohm resistance of the electrolyte, electrodes and conductors; $\eta_{conc}(I)$ is an exponential term (diffusion or concentration over-potential), which represents the lose due to reactants reactivity variation on interface, important for high values of current density.

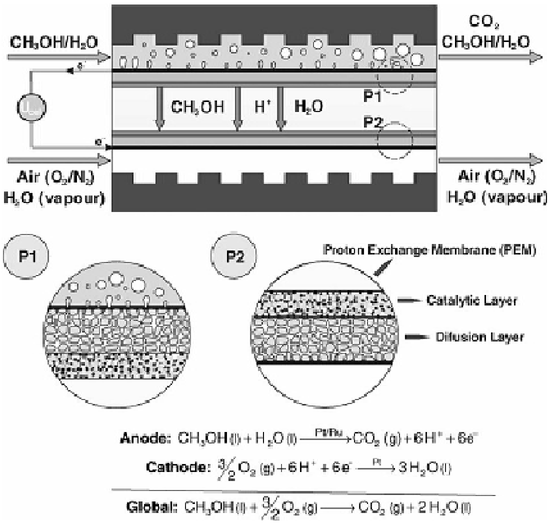

Figure.1. Image of a DMFC: water, methanol and protons change membrane (PEM)

For a thermal engine the maximum theoretic efficiency is that of a Carnot cycle:

$$\eta_C=1 - T_2/T_1, \qquad (5)$$

where T_1 and T_2 are absolute temperatures of hot source and cold source respectively; for combustion cell, maximum efficiency is expressed by the ratio between free energy Gibbs (ΔG) and the variation of free enthalpy (ΔH) in electrochemical reaction:

$$\eta_{pc}= \Delta G/\Delta H\,. \qquad (6)$$

The global conversion efficiency of a combustion cell is superior to that of a thermal engine.

Thermodynamics of transformations chemical energy – electric energy give:

$$-\Delta G = L_{util}, \qquad \Delta G = \Delta H - T\Delta S \quad (7)$$

The work-function of the electrical charge is giving by relation:

$$L_{util} = nF\Delta E \qquad or \qquad -\Delta G = nF\Delta E \quad (8)$$

where, n=number of electrons participating in reaction, E = e.m.f. (V) (electromotive force), F = Faraday's constant.

The heat produced is given by the relation:

$$Q = T\Delta S = \Delta H - \Delta G. \quad (9)$$

For a general chemical reaction:

$$\Delta G = \Delta G^0 + RT\ln\frac{[C]^c[D]^d}{[A]^a[B]^b} \quad (10)$$

which could be written for an ideal gas,

$$\Delta G = \Delta G^0 RT\ln\frac{\prod(part.prod.)^{\nu_i}}{\prod(part.react.)^{\nu_i}} \quad (11)$$

where ΔG^0 is Gibbs free energy in standard conditions (*P=760mmHg, T=25C°C*), ν_i are stoichiometric coefficients of reaction.

Assuming that: $-\Delta G = nF\Delta E$, on obtains:

$$E = E_0 + RT\ln\frac{\prod(react.part)^{\nu_i}}{\prod(prod.part)^{\nu_i}} \quad (12)$$

For standard conditions it follows, $E = E_0$.

In irreversible thermodynamics there are loses due to: 1. Ohmic polarization – due to resistance phenomena when ions pass through electrolyte and electrons pass through interface. 2. Concentration polarization – due to quickly consumption of reactants on electrodes surface and appearing of concentration gradients. 3. Activation polarization – refers to surpass of a initial threshold potential ΔV_{act} similar with the case of concentration polarization.

The efficiency is defined after the relation:

$$\eta = \frac{L_{el}}{LHV} = \frac{L_{el}/nF}{LHV/nF} = \frac{E}{E_{LHV}} \quad (13)$$

LHV represents the heat obtained by combustion of a mol of combustible (*J/mol* combustible). E_{LHV} represents the electric equivalent of caloric inferior power of the combustible.

Then the potential difference of the cell is:

$$V_c = E - \Delta V_{ohm} - \Delta V_{conc} - \Delta V_{act}. \quad (14)$$

Here, ΔV_{ohm} represents potential drop due to electric resistance of the cell, ΔV_{conc} potential drop due to concentration variation and ΔV_{act} potential drop due to initial activation processes. Subsequent sources of losing are bonded by the way of using combustible and air.

$$U_{comb} = \frac{m_{H_2,cons}}{m_{H_2,in}} \qquad or \qquad (15)$$

$$U_{comb} = \frac{m_{CH_3OH,cons}}{m_{CH_3OH,in}}. \quad (16)$$

Here U_{comb} is the ratio which describes the efficiency of combustible utilization, and *m* are masses of combustibles consumed, and initial masses respectively. It follows that:

$$\eta = \frac{V_c U_{comb}}{E_{LHV}}. \quad (17)$$

If one particularizes electrochemical oxidation of methanol, it follows assuming that *a=1, b=3/2, c=1* and *d=2,*

$$\Delta G = \Delta G^0 + RT\ln\frac{[CO_2]^1[H_2O]^2}{[CH_3OH]^1[O_2]^{3/2}} \quad (18)$$

fact which diminishes ΔG comparing with ΔG^0, and consequently a decreasing of efficiency. As a general rule, valid for combustion cells, the removal of formed water should be ensured, because it induces a decrease of methanol solution concentration. In this case, of direct methanol fuel cell, it works with totally immersed electrodes, which simplify the problem from the mechanical point of view. Ideal condition consists of complete penetration of electrolyte into porosity of the electrode. It is pointed to obtain a higher percent of volume porosity, pores-free. The dimension of particles have to be chosen to obtain a good contact through them and with support layer, in order to facilitate electronic conductibility in all electrode volume [9,10,11].

The reaction rate in the pores of the electrode, in every point, is dependent by interface potential, current density which flows through interface electrode-electrolyte; by the concentration of reactant species which arrive in pores, and by nature of electro-catalyzer deposited on electrode. These local conditions are depended by mass transfer of reactant species and by current transport to a specified point and by this point to another interface. So, to make a complete characterization of the porous electrode it is necessary to know the distribution of reaction in all electrode volume.

A *calculus example* is presented here:

Global reaction:

$$CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2H_2O$$

For ideal conditions:

$M_{CH_3OH} = 32Kg / Kmol$;

$M_{O_2} = 32Kg / Kmol$

On anode:

$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

So, every CH_3OH molecule produces $6e^-$.

1Kmol CH_3OH :

$Q = N_A \bullet e \bullet 6$;

$Q = 5{,}78208 \cdot 10^8 C$

Total produced energy is (U=1,21V)

$W = Q \cdot U = 6{,}99...\cdot 10^8 J$ Or,

$W = 194{,}3\ kWh$

For real conditions:

$U = 0{,}82\ V$ (from literature)

5% lost by intermediate reactions, so the efficiency, $\eta_{metanol} = 95\%$

$$Q = N_A \bullet e \bullet 6 \bullet 0{,}95 = 5{,}492... \quad 10^8 C$$

$$W = Q \bullet U = 5{,}492... \quad 10^8 \quad 0{,}82 =$$

$$= 4{,}5 \bullet 10^8\ J = 125kWh$$

$$\eta_{energetic} = \frac{W_{real}}{W_{ideal}} = \frac{125kWh}{194{,}3kWh} = 64\%$$

References

1. H. Dohle, J. Divisek and R. Jung, Process engineering of the direct methanol fuel cell, *J. Power Sources* **86** (2000), pp. 469–477

2. H. Dohle, H. Schmitz, T. Bewer, J. Mergel and D. Stolten, Development of a compact 500W class direct methanol fuel cell stack, *J. Power Sources* **106** (2002), pp. 313–322

3. D.H. Jung, C.H. Lee, C.S. Kim and D.R. Shin, Performance of a direct methanol polymer electrolyte fuel cell, *J. Power Sources* **71** (1998), pp. 169–173.

4. Muscalu, S., Platon,V., *Pile de combustie*, Editura Tehnica, 1989

5. S.R. Narayanan, A. Kindle, B. Jeffries-Nakamura, W. Chun, H. Frank, M. Smart, T.I. Valdez, S. Surampudi, G. Halpert, J. Kosek and C. Cropley:, Recent advances in PEM liquid-feed direct methanol fuel cells, *Ann. Battery Conf. Appl. Adv.* **11** (1996), p. 113.

6. N. Nakagawa and Y. Xiu, Performance of a direct methanol fuel cell operated at atmospheric pressure, *J. Power Sources* **118** (2003), pp. 248–255.

7. A.K. Shukla, P.A. Christensen, A.J. Dickinson and A. Hamnett:, A liquid-feed solid polymer electrolyte direct methanol fuel cell operating at near ambient conditions, *J. Power Sources* **76** (1998), pp. 54–59.

8. A.K. Shukla, C.L. Jackson, K. Scott and G. Murgia, A solid-polymer electrolyte direct methanol fuel cell with a mixed reactant and air anode, *J. Power Sources* **111** (2002), pp. 43–51.

9. S. Surampidi, S.R. Narayanan, E. Vamos, H. Frank, G. Halpert, A. LaConti, J. Kosek, G.K. Surya Prakash and G.A. Olah, Advances in direct oxidation methanol fuel cells, *J. Power Sources* **47** (1994), pp. 377–385.

10. T.I. Valdez, S.R. Narayanan, Recent studies on methanol crossover in liquid-feed direct methanol fuel cells, Proceedings of the 194th Meeting of the Electrochemical Society, Boston, November 1998.

11. Veziroglu, T., N., *International Journal of Hydrogen Energy*, 2000, 1143