Contribution sharing of a fuel mixture components to the fuel cell potential of a Direct Alcohol Fuel Cell

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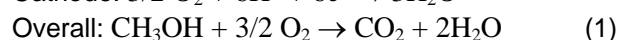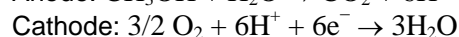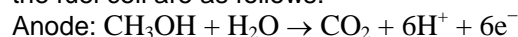(*) corresponding author: teresa.leo.mena@upm.es

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1 Introduction

The increasing worldwide demand for electricity impels to develop clean and renewable energy resources. In the field of portable power devices not only size and weight represent important aspects to take into account, but the fuel and its storage are also critical issues to consider. In this last sense, the direct methanol (MeOH) fuel cells (DMFC) play an important role as they can offer high power and energy density, low emissions, ambient operating conditions and fast and convenient refuelling. Recently, other liquid fuel, ethanol (EtOH), is attracting interest and direct ethanol fuel cells (DEFC) are being developed [1]. But despite the evident advantages of EtOH, that can be easily produced in great quantity from renewable sources, presents much lower toxicity than MeOH and has high power density, its electrochemical oxidation features makes the performance of DEFC to be rather low. The possibility of using MeOH and EtOH together in a direct alcohol fuel cell (DAFC) would lead to take profit of the advantages of both alcohols and the objective of this work is to study the behaviour of a DAFC when the fuel is a mixture of MeOH and EtOH.
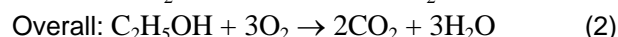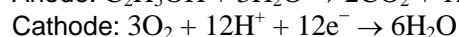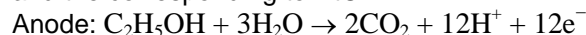
This possibility has been theoretically investigated by developing a comparative exergy study of a DAFC fed with MeOH/EtOH mixtures against the same fuel cell fed with either MeOH or EtOH alone [2]. A simple model to calculate the polarization curves corresponding to binary aqueous alcohol mixtures has been proposed and polarization curves exhibiting sharp steps, corresponding to the current density values at which anode limiting current densities are attained, have been predicted. This study concluded that a relative maximum of power could be obtained by using a fuel mixture of MeOH and EtOH with a relatively low proportion of MeOH, being this mixture the unique curve with no sharp step, showing an aspect similar to that of a polarization curve of single MeOH or EtOH. Up to the author's knowledge, no experimental work has been performed using alcohol blends as fuel of fuel cells.

In this work, the experimental polarization curves of a single DAFC fed by aqueous MeOH, aqueous EtOH and a series of aqueous MeOH−EtOH blends have been measured. The objective is to study the fuel cell performance under a variety of fuel compositions and investigate the possibility of taking profit of the advantages of both alcohols.

The reactions taking place at the electrodes and the overall current-producing reaction of MeOH in the fuel cell are as follows:

Anode: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$
Cathode: $3/2\ O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$
Overall: $CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2H_2O$ (1)

and the corresponding to EtOH:

Anode: $C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$
Cathode: $3O_2 + 12H^+ + 12e^- \rightarrow 6H_2O$
Overall: $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$ (2)

2 Experimental

2.1 Experimental setup

The experimental setup and the single fuel cell used have been described in a previous work [3], as well as the equipment used to perform electrochemical measurements. Bipolar plates have been fabricated on 316SS.

2.2 Electrodes

The electrodes, with an active area of 5 cm^2, have been prepared by QuinTech e.K. The anode, GDE Freudenberg H2315 I3C1, contains a total PtRu loading of 3 mg cm^{-2} onto GDL Freudenberg H2315 I3C1. The cathode, GDE Freudenberg H2315 T10A, contains a total Pt loading of 3 mg cm^{-2} onto GDL Freudenberg H2315 T10A.

2.3 Polarization curves

One series of polarization curves has been registered in a single direct alcohol fuel cell. The fuel consists of liquid MeOH/EtOH mixtures in water at 1 mol L^{-1} constant total alcohol concentration. To register the series, the alcohol mixture composition has been varied gradually from MeOH 1 mol L^{-1} to

EtOH 1 mol L^{-1}. Intermediate MeOH/EtOH molar compositions investigated have been 0.90/0.10; 0.70/0.30; 0.50/0.50; 0.30/0.70; 0.10/0.90. The oxidant has been always pure oxygen. The temperature of the fuel cell has been kept constant at 80 ºC in every case. Before any test, the cell has been preconditioned (it is always run under constant load, 0,150mV, and operation conditions over 15 minutes) for three times. The polarization curve corresponding to each different fuel composition has been also registered for three times.

The experimental conditions used are shown in Table 1.

Table 1. Experimental conditions of measurements.

Parameter	Units	Value
Alcohol (MeOH−EtOH) concentration	mol L^{-1}	1.0
Alcohol flow rate	mL min^{-1}	3.0
Oxygen flow rate	mL min^{-1}	250
Oxygen pressure	bar	1.0
Temperature	ºC	80

3 Polarization curves model

3.1 The polarization curve when the fuel is a single alcohol

The model used to describe the polarization curve of a single aqueous alcoholic solution is described in [2] and references therein, and is based on several studies involving DAFC [4].

The main equations used to model the polarization curve when the fuel cell is fed by a single aqueous alcoholic solution are summarized in the following paragraphs.

The general expression of a fuel cell polarization curve can be written as:

$$V = E - \eta_{act,a} - \eta_{act,c} - \eta_{conc,a} - \eta_{conc,c} - \eta_{ohmic} \qquad (3)$$

where E stands for the Nernst potential in the operating conditions:

$$E = E^0 + \frac{RT}{z_a F} \ln\left(\frac{c_{CO_2}^{v_{CO_2}}}{c_{alc} c_{O_2}^{v_{O_2}}} \right) \qquad (4)$$

When the alcohol is MeOH $v_{CO_2} = 1$, $v_{O_2} = 3/2$ and $z_a = 6$, but if the fuel is EtOH $v_{CO_2} = 2$, $v_{O_2} = 3$ and $z_a = 12$, , as derived from equations (1) and (2), respectively. c_{alc} is the fuel concentration in the catalytic layer, calculated with the solution to the diffusion equations proposed in [5].

The crossover rate r_c is calculated as:

$$r_c = \frac{\left(j_{lim}^a - j \right)\left(\beta + n_d \, j/j_w \right)}{j + j_{lim}^c \left(\beta + n_d \, j/j_w \right)} \qquad (5)$$

$$\beta = \frac{D_m l_b^a}{D_b^a l_m} \qquad j_w = F D_b^a \frac{w^a}{l_b^a}$$

being w^a the water molar concentration and j_{lim}^a, j_{lim}^c stand for the anode and cathode limiting current densities, respectively:

$$j_{lim}^a = z_a F \frac{D_b^a c_h^a}{l_b^a}, \quad j_{lim}^c = 4F \frac{D_b^c c_h^c}{l_b^c} \qquad (6)$$

where c_h^a stands for the inlet alcohol concentration, l_b^a, l_b^c are the thicknesses of the anode and the cathode backing layers, respectively, and D_b^a, D_b^c represent the diffusion coefficient of alcohol and oxygen in their respective backing layers.

The anodic and cathodic activation overvoltages as a function of the exchange current density j_0 and the parameter α have the following expressions:

$$\eta_{act,a} = \frac{RT}{z_a \alpha_a F} \ln \frac{j}{j_{0,a}}; \ \eta_{act,c} = \frac{RT}{z_c \alpha_c F} \ln \frac{j}{j_{0,c}} \qquad (7)$$

Table 2. Assumed parameter values for MeOH and EtOH.

Parameter	MeOH	EtOH
E^0	1.214	1.146
z_a	6	12
l_m (cm) [6]	0.0178	0.0178
l_b (cm) [6]	0.0300	0.0300
l_c (cm) [8]	0.0020	0.0020
Cathode transfer coeff. α_c [7, 8]	1	1
n_d [8]	3.16	3.16
$D_b^c \left(cm^2 \cdot s^{-1} \right)$ [9]	0.338	0.338
γ_c [7,8]	1[6]	1
$A_v j_0^{ref}$	[7]	[8]
$j_{0,c} \left(A \cdot cm^{-2} \right)$ [10]	$1.87 \cdot 10^{-8}$	$1.87 \cdot 10^{-8}$
$D_b^a \left(cm^2 \ s^{-1} \right)$ [11]	$2.984 \cdot 10^{-5}$	$2.984 \cdot 10^{-5}$
$D_m \left(cm^2 \ s^{-1} \right)$	$2.148 \cdot 10^{-5}$ [12]	$2.97 \cdot 10^{-5}$ [9]

The concentration overvoltage is calculated following the expressions:

$$\eta_{conc,a} = \frac{RT}{z_a F} \ln\left(\frac{j_{lim}^a}{j_{lim}^a - j - j_{cross}} \right) \qquad (8)$$

$$\eta_{conc,c} = \frac{RT}{z_c F} \ln\left(\frac{j_{lim}^c}{j_{lim}^c - j - j_{cross}} \right)$$

where j_{lim} and the flux of alcohol through the membrane, expressed in current density units, j_{cross}, are calculated as in [4]. The ohmic overpotential is ex-

pressed as $\eta_{\text{ohmic}} = Rj$, where R stands for the sum of membrane and contact resistance times area. The anode exchange current density $j_{0,a}$ can be estimated as a function of the anode reaction order γ_a and the alcohol concentration in the catalytic layer c_{alc}.

The fixed parameters assumed in the model, for MeOH and EtOH, are shown in Table 2.

3.2 The polarization curve when the fuel is a mixture of alcohols

To develop this study the total alcohol concentration and the volumetric flow rate at the fuel cell inlet are kept constant, thus the molar flow rate of alcohol $\dot{n}_{in} = \dot{n}_{M,in} + \dot{n}_{E,in}$ entering the fuel cell is kept constant. Then, the proportion of MeOH, y_M, in the mixture can be expressed as $y_M = \dot{n}_{M,in} / \dot{n}_{in}$ and that of EtOH, $y_E = \dot{n}_{E,in} / \dot{n}_{in}$. Therefore, $y_M + y_E = 1$.

Three possible models have been proposed to study the behaviour of polarization curves corresponding to a DAFC fed with a fuel consisting of aqueous MeOH/EtOH blends.

3.2.1 Model I
Each alcohol contributes independently to the total cell voltage:

$$V = y_M V_M \left(\vec{P}_M, j, y_M c \right) + y_E V_E \left(\vec{P}_E, j, y_E c \right) \qquad (9)$$

where c is the total alcohol concentration and $\vec{P}_i$ is the parameter set of alcohol i (those collected in Table 2 and γ_a, α_a and R).

3.2.2 Model II
A total cell voltage is calculated with averaged parameters, that is, the cell voltage is assumed to result from an "averaged pure fuel":

$$V = V \left[\left(y_M \vec{P}_M + y_E \vec{P}_E \right), j, c \right] \qquad (10)$$

3.2.3 Model III
This model is similar to Model II, but parameters γ_a, α_a and R are assumed as unique (they are not averaged) for each MeOH/EtOH mixture. Therefore, they are fitted in each case.

4 Results and discussion

Performance of the DAFC under study fed with different MeOH/EtOH aqueous solutions is shown in Fig. 1. Experimental polarization and power density curves of the single fuel cell operating with a fuel consisting of 1M aqueous solution of: pure MeOH; 90% MeOH/10% EtOH; 70% MeOH/30% EtOH; 50% MeOH/50% EtOH; 30% MeOH/70% EtOH; 10% MeOH/90% EtOH and pure EtOH are depicted in Fig. 1. As observed, the fuel performance diminishes gradually from pure MeOH to pure EtOH. Even at a low EtOH concentration,

y_{EtOH}=0.1 and y_{MeOH} =0.9, EtOH affects in a significant way the behaviour of the fuel cell.

Polarization curves corresponding to pure MeOH and pure EtOH have been fitted to the model described in Subsection 3.1. The results obtained for pure alcohols are collected in Table 3.

Figure 2 shows the results obtained by using Model I to describe the performance of the single DAFC.

Table 3. Fitting parameters of the $V–j$ model used for MeOH and EtOH.

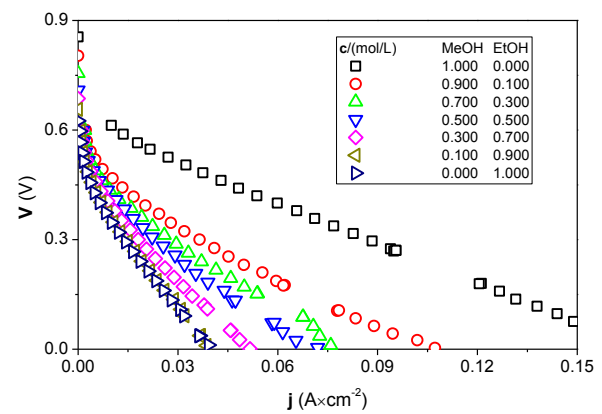| Parameter	γ_a	α_a	R ($\Omega\ \text{cm}^2$)
MeOH	0.8147	0.1439	3.2852
EtOH	0.6346	0.0478	9.0140

Fig. 1. The performance comparison of a DAFC fed with MeOH/EtOH aqueous solutions. Total alcohol concentration 1 M. Temperature 80 ºC.
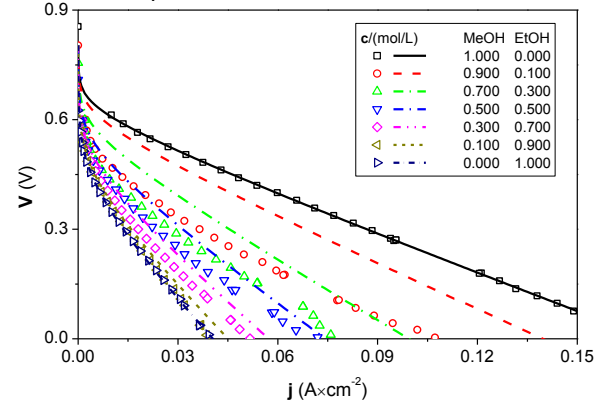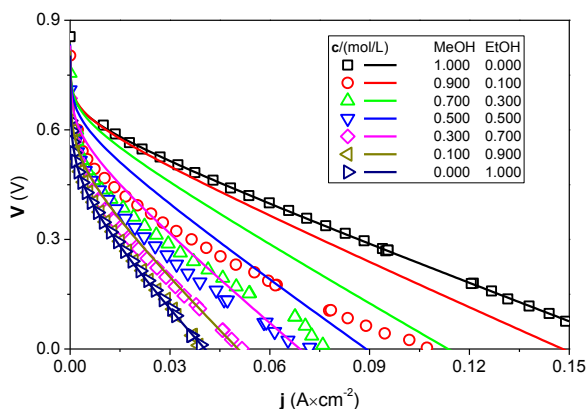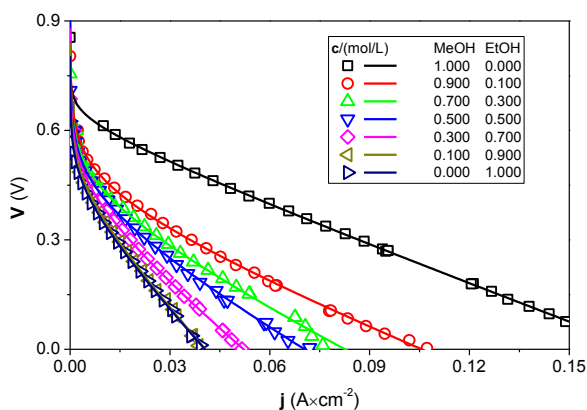

Fig. 2. Experimental and Model I fitted V-j curves of a DAFC fed with aqueous MeOH/EtOH mixtures at 80 ºC and 1M total alcohol concentration.

Figure 3 shows the results obtained by using Model II to describe the performance of the single DAFC.

Finally, the results from fitting the experimental $V–j$ curves to Model III are depicted in Fig. 4 and the parameter values of γ_a, α_a and R derived for each mixture are collected in Table 4. The results are quite satisfactory in this case, and it seems that the aqueous alcohol mixture behaves as a "pure averaged alcohol".

Fig. 3. Experimental and Model II fitted *V-j* curves of a DAFC fed with aqueous MeOH/EtOH mixtures at 80 ºC and 1M total alcohol concentration.

Fig. 4. Experimental and Model III fitted *V-j* curves of a DAFC fed with aqueous MeOH/EtOH mixtures at 80 ºC and 1mol L^{-1} total alcohol concentration.

Table 4. Fitted parameters of the *V−j* model for aqueous MeOH/EtOH mixtures.

MeOH /EtOH ratio	γ_a	α_a	R (Ω cm^2)
9:1	0.5173	0.0868	3.2986
7:3	0.5389	0.0718	4.1787
5:5	0.5339	0.0615	4.8116
3:7	0.5630	0.0551	6.8815
1:9	0.6042	0.0505	9.1881

5 Conclusions

To investigate the possibility of using direct alcohol fuel cells fed with alcohol mixtures, an experimental study of polarization curves of a direct alcohol fuel cell fed with alcohol mixtures has been performed.

As it can be expected, MeOH/water solution yields the best performance, since this fuel cell has been designed and developed to work with MeOH.

The fuel cell performance decreases as the EtOH content increases. It becomes worse respec to the reaction kinetics and to the protonic conductivity, as it can be deduced from the models fitting results.

Models I and II show that the cell behavior, when it is fed with alcohol mixtures, does not respond to concentration differences and the mixture does not seem to be an alcohol whose properties vary proportionally to the MeOH/EtOH rate.

The results are quite satisfactory for model III, and it seems that the aqueous alcohol mixture behaves as a "pure averaged alcohol".

6 Acknowledgements

7 References

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