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(54) Title: METHOD AND APPARATUS FOR MEASURING INTERFACE REACTANT CONCENTRATION IN AN ELECTRO-CHEMICAL DEVICE

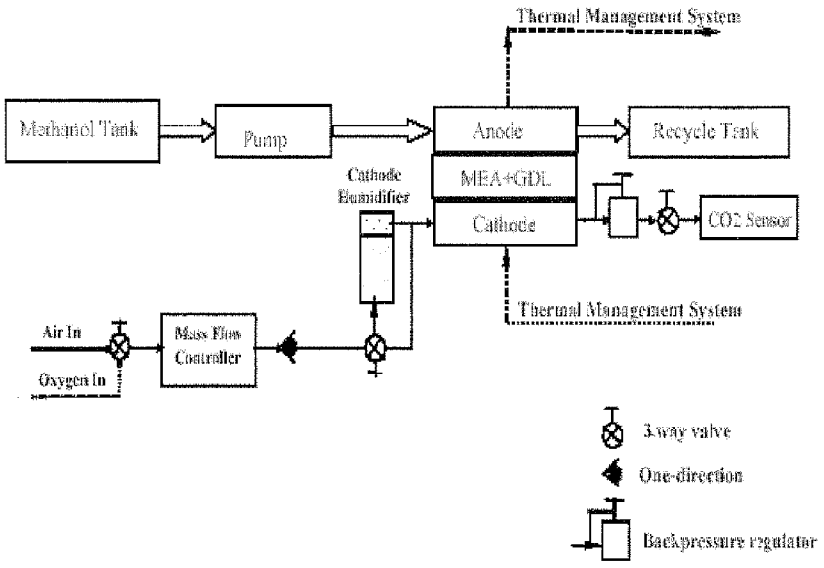

Figure 1.

(57) Abstract: A measuring method for determining the interface fuel concentration and/or the drag coefficient of a fuel cell at I_1 based on measuring transient fuel crossover rate and post change current density as the current of the fuel call is abruptly changed (1) from I_1 to I_2 and (2) from I_1 to I_3 wherein I_1, I_2, and I_3 are each of a different value. The post change current density is (a) the current density at I_2 after the I_1 to I_2 transition or (2) the current density at I_3 after the I_1 to I_3 transition. Where the fuel cell is a direct methanol fuel cell (DMFC), the interface fuel concentration is the interface methanol and the drag coefficient is the methanol drag coefficient.

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METHOD AND APPARATUS FOR MEASURING INTERFACE REACTANT CONCENTRATION IN AN ELECTRO-CHEMICAL DEVICE

RELATED APPLICATIONS

This application claims the benefit of priority to United States Application 60/929,555 filed July 3, 2007 the disclosure of which is incorporated by reference in its entirety.

BACKGROUND

Direct methanol fuel cell (DMFC) is a promising energy conversion device for the future. However, methanol crossover from the anode to the cathode is a serious problem that severely reduces the cell voltage, current density, fuel utilization and hence the cell performance. Since methanol can be dissolved into water to any degree and the commonly used solid polymer electrolyte, Nafion®, readily absorbs water as well as methanol, methanol crossover is thus unavoidable with the current DMFC technology.

Methanol crossover in a DMFC includes three parts, the diffusion part, the electro-osmosis part and the penetration part caused by the pressure difference between the anode side and cathode side of the electrolyte membrane. All of these three parts are directly related to the methanol concentration at the interface between the anode catalyst layer and the electrolyte membrane. The methanol concentration at this interface is also a direct criterion for the total catalytic performance of the anode catalyst layer. The ratio among the carbon(graphite), catalyst and electrolyte, the manufacture techniques which determine the structure of catalyst layer, all these effectors effect the methanol concentration at this interface and so is the cell performance. Some physical experiments [1,2] and mathematical model simulations [3,4] have been conducted to study the performance of a DMFC, however, none of them found a way to obtain the methanol concentration at this interface due to the physical space limited or a lack of detailed study on the transition states of a running DMFC.

BRIEF SUMMARY OF THE INVENTION

One embodiment of the invention is directed to a method for measuring an interface fuel concentration (interface reactant concentration) and a fuel drag coefficient in an electro-chemical device – such as a fuel cell. The method involves a first step of measuring a first transient fuel crossover rate and a first post change current density of the fuel cell as the fuel cell transitions from one current density (I_1) to a second different current density (I_2). The second step involves measuring a second transient fuel crossover rate and a second post change current density of the fuel cell as the fuel cell transitions from one current density (I_1) to a third different current density (I_3). In the third step, an interface fuel concentration and a fuel drag coefficient is determined based on the previously collected measurements (first and the second transient fuel crossover rate and the first and the second post change current density). In this method, I_1, I_2 and I_3 are each of a different value but they can be of any relation to each other.

The transient fuel crossover rate (see, e.g., Figure 3) may be a peak when current is increased or may be a valley (a dip, a local depression) when the current is decreased. For example, as current is increased, the fuel crossover rate can suddenly increase to a peak (Figure 3) before settling to a new lower value. As another example, as current is decreased, the fuel crossover rate can suddenly decrease to a valley, before settling to a new higher value (Figure 3). In other words, the first transient fuel crossover rate or the second transient fuel crossover rate can be determined by measuring a peak value of transient fuel crossover as the fuel crossover rate is decreased, or by measuring a trough value of transient fuel crossover as the fuel crossover rate is increased. The transient fuel crossover rate can be measured by measuring CO_2 concentration at the cathode side of the fuel cell

In a preferred embodiment, I_1, I_2 and I_3 are positive values denoting the regular flow of current from a fuel cell. Further, I_1, I_2 and I_3 may be each less than I_{max}, the maximal current through the fuel cell. As other examples, the relationship between I_1, I_2 and I_3 may be $I_2 < I_1 < I_3$; or $I_1 < I_2 < I_3$; or $I_3 < I_1 < I_2$; or $I_1 < I_3 < I_2$; or any other relationship as long as the condition that $I_1 \neq I_2$, $I_2 \neq I_3$ and $I_1 \neq I_3$ are satisfied. The accuracy of the method or the ease in measurement is improved if I_1, I_2 and I_3 are significantly different.

In a preferred embodiment, I_1, I_2 and I_3 are at least 10% apart. That is, for example, if I_1 is 100, I_2 and I_3 should be greater than or equal 110 or less than or equal to 90. Furthermore, if I_2 is 110, I_3 should be greater than or equal to 121, or less than or equal to 90 (so I_3 is at least 10% apart from both I_2 and I_1.). In another preferred embodiment, I_1, I_2 and I_3 are at least 20%, 30%, 40% 50% 75% or 100% apart. As another example I_1, I_2 and I_3 at 100% apart could have values of 50, 100, and 200.

The electrochemical device may be a fuel cell. The fuel cell may comprise an anode catalyst layer, a cathode catalyst layer, and at least one layer of electrolyte. Further, the electrolyte can be a liquid electrolyte, an electrolyte membrane, or a solid electrolyte. The interface fuel concentration to be measured may be a concentration of fuel (reactant) between the anode catalyst layer and the electrolyte. In addition, the fuel cell can comprise an anode diffusion layer, a cathode diffusion layer or both.

The fuel cells that are susceptible to the measurement methods of the invention may be a liquid fuel cell. In another aspect, the fuel cell can be a polymer electrolyte membrane fuel cell, a phosphoric acid fuel cell, a direct methanol fuel cell, an alkaline fuel cell, a solid oxide fuel cell or a molten carbonate fuel cell. The fuel cell may use an organic fuel – such as, for example, methanol for a direct methanol fuel cell DMFC. If a DMFC is measured, the interface fuel concentration is an interface methanol concentration, and the drag coefficient is a methanol drag coefficient.

In a preferred embodiment, the fuel cell being measure has the same pressure on an anode side and on a cathode side.

Another embodiment of the invention is directed to an apparatus for determining an interface fuel concentration or a fuel drag coefficient in a fuel cell. The method of measurement is described throughout the specification such as in the preceding paragraphs of this section. The apparatus may comprise (a) means for measuring a transient fuel crossover rate in the fuel cell; (b) means for measuring a current density of the fuel cell; and (c) means for changing a current density of the fuel cell in a stepwise fashion between I_1, and I_3, and between I_2 and I_3. Part (a) can be a CO_2 detector on the cathode side of the fuel cell to determine CO_2 percentage and a flow meter to determine total gas per unit time. Part (b) can be an amp meter, a voltmeter or any electronic device that can measure electric current. Part (c) can be a load bank, a voltage controller, or a

power supply. It is preferred that part (c) be capable of switching the current density quickly – that is, the current density should change as close to a step function as possible.

The apparatus may further comprise a processor, such as a computer or dedicated detector, adapted to receive the signals from the means for measuring a transient fuel crossover rate and the means for measuring a current density. Based on these inputs, the processor should calculate the interface fuel concentration or the fuel drag coefficient. The processor may contain other means for user input or automatic input for parameters such as membrane area – used to determine current density (current density = total current/area).

Another aspect of the invention is directed to a fuel cell comprising the apparatus. In this aspect, the apparatus can monitor the interface reactant concentration (e.g., interface methanol concentration). For example, if the interface reactant concentration is at an undesirable level, operating parameters may be adjusted to bring the concentration back to an acceptable level. Adjustments may involve using auxiliary power from a generator or battery, stopping the fuel cell, increasing or reducing the load – for example, by adding or removing fuel cells - or other types of adjustments and changing the fuel concentration.

A direct methanol fuel cell may be used for any of the embodiments and aspects of this disclosure. Any fuel feedstock may be used such as for example, methanol at concentrations of 0.5 M to 5M. However ranges of methanol above and below these values are also applicable.

It is understood that in the context of an electrochemical device such as a fuel cell, the fuel is one of the reactants.

These and other features and advantages will be better and more completely understood by referring to the following detailed description of exemplary non-limiting illustrative embodiments in conjunction with the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 depicts a schematic of experimental system.

Figure 2 depicts a schematic of peaks for transient methanol crossover measurement

Figure 3 depicts methanol crossover peaks at transient states: methanol concentration 0.5M; methanol flow rate, 3 $ml\,min^{-1}$; air flow rate, 800 sccm.

Figure 4 depicts methanol crossover peaks at transient states: methanol concentration 1M; methanol flow rate, 3 $ml\,min^{-1}$; air flow rate, 800 sccm.

Figure 5 depicts methanol crossover peaks at transient states: methanol concentration 2M; methanol flow rate, 3 $ml\,min^{-1}$; air flow rate, 800 sccm.

Figure 6 depicts methanol crossover peaks at transient states: methanol concentration 3M; methanol flow rate, 3 $ml\,min^{-1}$; air flow rate, 1600 sccm.

Figure 7 depicts methanol crossover peaks at transient states: methanol concentration 0.5M; methanol flow rate, 3 $ml\,min^{-1}$; air flow rate, 1600 sccm.

Figure 8 depicts methanol drag coefficient versus methanol concentration at the interface between the anode catalyst layer and electrolyte polymer membrane (linear model).

Figure 9 depicts methanol drag coefficient versus methanol concentration at the interface between the anode catalyst layer and electrolyte polymer membrane (Weibull Model)

Figure 10 depicts the effects of the cell voltage and methanol feeding concentration on the total amount of methanol crossover and the amount of methanol crossover caused by the diffusion and electro-osmosis drag: no cathode humidification; methanol concentration 0.5-5M; methanol flow rate, 3 $ml\,min^{-1}$, air stoichiometric is greater than 40.

Figure 11 depicts the effects of methanol feeding concentration on the total methanol crossover and the amount of methanol crossover caused by the diffusion and osmosis drag: methanol concentration 0.5-5M; methanol flow rate, 3 $ml\,min^{-1}$, air stoichiometric is greater than 40, Cell voltage is at V_{max}.

Figure 12 depicts the effects of methanol feeding concentration on the total methanol crossover and the amount of methanol crossover caused by the diffusion

and osmosis drag: methanol concentration 0.5-5M; methanol flow rate, 3 $ml\,min^{-1}$, air stoichiometric is greater than 40, Cell voltage is at 0.394V.

Figure 13 depicts the effects of methanol feeding concentration on the total methanol crossover and the amount of methanol crossover caused by the diffusion and osmosis drag: methanol concentration 0.5-5M; methanol flow rate, 3 $ml\,min^{-1}$, air stoichiometric is greater than 40, Cell voltage is at 0.096V.

DETAILED DESCRIPTION OF THE INVENTION

In this paper, the transition states of a DMFC when the cell voltage change abruptly are systematically studied. Based on the quantitatively analysis of the peaks in methanol crossover during different transition states. The methanol concentration at the interface between the anode catalyst layer and the electrolyte membrane are obtained and the mechanism behind are explained in details.

The experimental system is schematically shown in Figure1. The fuel cell test station was manufactured by Fuel Cell Technology, Inc. A major component of the test station is the HP® 6050A system DC electronic load controller, which is capable of controlling the electrical load on the fuel cell as well as measuring its voltage versus current responses. This experimental system also provides control over anode and cathode flow rates, cell operating temperature, operating pressure, and humidification temperature for the cathode. The cathode mass flow rate is controlled and measured by a MKS® mass flow controller, and the anode flow rate is controlled and measured by a peristaltic pump by Gilson, Inc.

The experimental fuel cell consists of two 316 stainless steel end plates, two graphite collector plates with machined serpentine flow fields, two carbon cloth diffusion layers, two catalyst layers and an electrolyte polymer membrane. The cell was kept at a constant temperature through the thermal management system during each experiment. The membrane used was Nafion® 117; the gas diffusion layers on the anode side is carbon cloth and ETEK ELAT® on the cathode side; the catalyst was Pt–Ru on the anode side with a loading of 4 mg cm^{-2}; and the catalyst was Pt-black on the cathode side with a loading of 4 mg cm^{-2}. The total active area of the cell was 5 cm^2. The carbon dioxide sensor used in this test was GMP221 Carbon dioxide probe from Vaisala Oyj, Finland.

When methanol reaches the cathode side, most reacts with oxygen and turns into CO_2, and only a very small amount becomes the intermediate products CH_xO_y and CO [5]. The concentration of water vapor at the cathode exit is a constant for each experiment since the temperature is held constant and the cathode exhaust is saturated. The method of using a carbon dioxide sensor to detect the amount of methanol cross-over is of sufficient accuracy for the measurements of this disclosure. In addition, it is very convenient and is capable of real time monitoring of methanol crossover as the measurements and experiments are conducted.

A series of experiments on the performance of a DMFC and corresponding methanol crossover have been conducted on transient states when the cell voltage is changed abruptly. The feeding methanol concentration for the DMFC tested ranges from 0.5M to 5M. Cell voltage changes for this series of experiments were performed according to the sequence of five voltage steps as follows: (1) V_{max} → (2) 0.394V → (3) 0.096V → (4) 0.394V → (5) V_{max}. Here V_{max} is the maximum cell voltage that can be detected in the DMFC in a closed circuit. At V_{max}, the cell current is 0.002A/cm^2 under our experimental conditions. There is a peak in the amount of methanol crossover every time when the cell voltage changes. For example, on Figure 4, when the voltage drops at about 0.14 hours, current density increases and a peak in methanol crossover occurs. Conversely, when the voltage is increased at 0.42 hours, there is a drop in current density and a dip (i.e., a local minimum, a valley) in methanol crossover is observed. Throughout this disclosure, it is understood that a "crossover peak" when the voltage drops and current increases also refers to a crossover dip or valley (i.e., a local minimum) when the voltage increases and the current decreases. The peak value also refers to the valley value (the transient minimum crossover) when the current is decreased. A fuel cell is understood to behave regularly – that is, when voltage is increased when current is decreased, voltage in decreased when current is increased, the maximum voltage (V_{max})occurs when the current is at the minimum and the minimum voltage (V_{min}) occurs when the current is at its maximum. The detailed analyze on these peaks and valleys will disclose a method of obtaining the methanol concentration at the interface between the anode catalyst layer and the electrolyte membrane.

In a working direct methanol fuel cell, the methanol crossover from the anode to the cathode is caused by the driving forces of concentration gradient, pressure gradient and electro-osmosis. The amounts of methanol crossover flux derived by all of these three affecters depend directly on the methanol concentration at the interface between the anode catalyst layer and the Nafion® electrolyte polymer membrane. Thus, if the fuel concentration (i.e., reactant concentration in a fuel cell, methanol concentration in a DMFC) is known, the amount of fuel crossover (e.g., methanol crossover) can be calculated using the methods of the invention. Considering the chemical dynamics for reactions occurring at the anode catalyst layer, it is reasonable to regard that that the rate of the methanol concentration changing at this interface is much slower than the rate of cell current change when a cell voltage changes abruptly. So when a cell voltage is changed to a new value, the cell current changes to a new value immediately while the methanol concentration at the interface between the anode catalyst layer and the Nafion® electrolyte membrane is still at the same value as under the previous cell voltage. It takes a little time for the concentration of methanol solution to reach a new balance with the present cell voltage. By studying these transient states when the cell voltage changes abruptly, we discovered a novel way of finding the value of different physical variants during this process, which include the methanol concentration at the interface between the anode catalyst layer and the Nafion® electrolyte membrane under different cell operating conditions, the electrochemical dynamics of methanol oxidation and methanol drag coefficient etc.

When the pressure gradient across the electrolyte membrane is equal to 0, the methanol crossover flux can be expressed by Equation (1),

$$j = -\frac{D\Delta c}{t} + \lambda_m \frac{I}{nF} \qquad (1)$$

Where D — the effective diffusivity of the Nafion® electrolyte membrane (m^2/s),

t — the diffusion structure thickness (For Nafion®117, $t = 0.018mm$),

F — Faraday constant F = 96485 C,

The validity of this method can be explained by the model that when the cell voltage changes abruptly, the cell current changes abruptly accordingly; while the methanol concentration at the interface between the anode catalyst layer and the

electrolyte membrane is still the same as when the cell is at the previous voltage. That is, the methanol crossover amount caused by the diffusion part is still the same as the diffusion part with the previous voltage, while the electro-osmosis part decreases or increases abruptly as the voltage changes and it takes a little time for the total methanol crossover to reach a new balance as shown in Figure 2.

The methanol crossover flux per active area is determined from the carbon dioxide concentration at cathode exit with Equation (2),

$$\bar{j} = \frac{Q \cdot X_{CO_2}}{6 \times 10^{-4} vA} \qquad (2)$$

where $\bar{j}$ — methanol mole flux per active area (mmol/(cm^{2}min)),

A— cell active area (cm^2) here A= 5 cm^2,

Q — cathode flow rate $Q = Q_c + Q_{H_2O}$ (sccm),

X_{CO_2} — carbon dioxide mole fraction at the cathode exit (%),

Q_c — cathode oxygen flow rate (sccm),

Q_{H_2O} — water vapor flow rate (sccm),

v — gas molar specific volume. v= RT/P, where P is pressure and R is gas constant, T is the temperature in K at the sensor position.

Due to the overflow of the cathode supply, we have Q = Q_c. When carrier gas flow rate is 800sccm, and $-\Delta C = C_i$, From Equation (1) and Equation (2), we have,

$$C_i D + 1.865575 \times 10^{-9} I \lambda_m = 3 \times 10^{-9} j \qquad (3)$$

where C_i means the methanol concentration at the interface between the anode catalyst layer and the electrolyte membrane. With the different methanol feeding concentration and different transition states when the cell voltage changes from one value to another one abruptly, different methanol crossover peaks are obtained and each peak corresponds to a special case of equation 3. The current density and methanol crossover flux for different peaks are shown in Table 1. Methanol diffusion coefficient in Nafion® electrolyte polymer membrane is $5.29 \times 10^{-10} m^2/s$ at 70°C [6] obtained with the original membrane thickness.

Table 1

Methanol feeding Con.(M)	0.5		1		2		3		5	
Current density I(A * cm^{-2}) vs methanol flux(mol * $cm^{-2}s^{-1}$)	I	j	I	J	I	j	I	j	I	j
Transient state 1	0.182	0.79036	0.156	1.576729	0.156	0.0337	0.102	0.054776	0.076	0.088532
Transient state 2	0.728	0.37355	0.847996	1.616421	0.888	0.050967	0.856	0.088903	0.696	0.134511
Transient state 3	0.23	0.16507	0.302	0.909595	0.282	0.032067	0.21	0.054005	0.116	0.090974
Transient state 4	0.001989	0.30037	0.002	1.043109	0.002	0.0278	0.002	0.047793	0.002	0.082977

Table 1. The cell current density and methanol flux corresponding to each peak during the transient states when cell voltage changes: methanol concentration 0.5-5M; methanol flow rate, 3 $ml\,min^{-1}$; transient state 1 represents the state when the cell voltage changes from Vmax to 0.394V; transient state 2 represents the state when the cell voltage changes from 0.394V to 0.096V; transient state 3 represents the state when the cell voltage changes from 0.096V to 0.394V; transient state 4 represents the state when the cell voltage changes from 0.394V to V_{max}; where V_{max} is the maximum cell closed circuit voltage where the cell current density is 0.002A/cm2.

Throughout this disclosure, DMFC and methanol concentrations have been used as an example. However, it should be understood that the general principal, the methods, the apparatus and the fuel cells of the invention is applicable to all fuel cells types.

While the technology herein has been described in connection with exemplary illustrative non-limiting implementations, the invention is not to be limited by the disclosure. The invention is intended to be defined by the claims and to cover all corresponding and equivalent arrangements whether or not specifically disclosed herein. All patents, patent applications and references cited in this disclosure are incorporated by reference in their entirety.

EXAMPLES

Example 1 Test results with methanol of 0.5M

Figure 3 shows that there are four peaks in methanol crossover corresponding to the four transition states when cell voltage is changed abruptly. The first peak is related to the cell voltage changes from V_{max} to 0.394V; the second peak is related to the cell voltage changes from 0.394V to 0.096V; the third peak is related to the cell voltage

changes from 0.096V back to 0.394V; the fourth peak is related to the cell voltage changes from 0.394V back to V_{max}. For each of these four peaks, we have one equation to calculate the methanol crossover peak value, there are

$$C_{i1}^{05}D+3.3953465\times10^{-10}\lambda_{i1}^{05}=2.37108\times10^{-11} \quad (4)$$

$$C_{i2}^{05}D+1.3581386\times10^{-9}\lambda_{i2}^{05}=1.12065\times10^{-11} \quad (5)$$

$$C_{i3}^{05}D+4.2908225\times10^{-10}\lambda_{i3}^{05}=4.9521\times10^{-12} \quad (6)$$

$$C_{i4}^{05}D+3.73115\times10^{-12}\lambda_{i4}^{05}=9.0111\times10^{-12} \quad (7)$$

These are four equations with eight unknowns. These equations may be solved by knowing the relationships among different unknown. Since both C_{i2}^{05} and C_{i4}^{05} are the interface methanol concentration when the cell voltage is equal to 0.394V and methanol feeding concentration is 0.5M, that is $C_{i2}^{05}=C_{i4}^{05}, \lambda_{i2}^{05}=\lambda_{i4}^{05}$. From Equation (5) and Equation (7), we have $\lambda_{i2}^{05}=1.62\times10^{-3}$, $C_{i2}^{05}=C_{i4}^{05}=0.017M$. According to the experimental results for methanol feeding concentration of 1, 2, 3 and 5M as shown in Figure 4, 5, 6 and 7, similarly, we have the values of the methanol concentrations at the interface between the anode catalyst layer and the electrolyte polymer membrane and the corresponding the methanol drag coefficients respectively when the cell voltage is 0.394V as listed in Table 2.

methanol feeding con.(M)	interface methanol con.(mM)	methanol drag coefficient (mol)
0.5	17.04	0
1	59.11	0.01
2	157.47	0.04
3	270.44	0.08
5	46.97	0.12

Table 2. Methanol crossover peaks at transient states at cell voltage of 0.394V: methanol concentration 0.5-5M; methanol flow rate, 3 $ml\,min^{-1}$.

Knowing the relationship between the variables, the equations can be solved and the interface fuel concentration (interface methanol concentration) and the drag coefficient can be found.

A more detailed explanation of the derivation of the interface fuel concentration and the fuel drag coefficient is shown in the last Example. These calculations may be used, of course, to derive the interface methanol concentration and the methanol drag coefficient.

Example 2 Derivation of the formula for methanol drag coefficient

Assume that when the cell temperature is kept constant, the methanol drag coefficient is only a function of the interface methanol concentration between the anode catalyst layer and the electrolyte membrane. Simulations with different mathematics models provide different relationships between the interface methanol concentration at the interface and the corresponding methanol drag coefficient. The relationship between them is fitted well by a linear model as shown in Figure 8. In Figure 8, the linear fit formula is

$$\lambda_m = kC_i \qquad (8)$$

Where k =14.94. This proves that the methanol drag coefficient is proportional to the methanol concentration at the interface between the anode catalyst layer and the electrolyte membrane. Mathematically a better fit could be obtained with a weibull model. The simulation results is shown in Figure 9, the Weibull Model formula is

$$\lambda_m = a + be^{cC_{i|ac/m}{}^d} \qquad (9)$$

Where a = 0.145, b = –0.145, c = –5.341, d = 1.489.

With introduction of the relationship between the methanol drag coefficient and the interface methanol concentration, the methanol concentration at interface between the anode catalyst layer and the electrolyte membrane in a DMFC can be obtained by introducing Equation (9) to Equation (4) and (6) when the methanol feeding concentration is 0.5M. Other results under different operating conditions are listed in Table 3.

Methanol feeding Con. (M)		0.5M	1M	2M	3M	5M
$C_{m\|ac/m}$ (mM)	V_{max}	40.8	80.1	166.5	281.7	470

	0.394	17.04	59.11	157.47	270.44	469.73
	0.096	8.9	44.1	144.6	252.8	467.2
Current	V_{max}	2	2	2	2	2
density	0.394	240	235	255	185	133
(mA/cm^2)	0.096	625	848	865	791	626

Table 3. Interface methanol concentration versus different methanol feeding concentration: no cathode humidification; methanol concentration 0.5-5M; methanol flow rate, 3 $ml\,min^{-1}$, air stoichiometric is greater than 40.

Based on the simulated methanol concentration at the interface, the differences between the simulated methanol crossover amounts from the experimental ones can be obtained for the steady states. The results are listed in Table 4 and they can be used to verify the validity of this assumption. Table 4 shows that the maximum error caused by the simulated procedures is of 11.15%. It supports the validity of this assumption. It is reasonable assumption based on which to study the methanol drag coefficient, the methanol concentration at interface between the anode catalyst layer and the electrolyte membrane in a DMFC.

Methanol feeding Con.(M)		0.5M	1M	2M	3M	5M
V_{max}	Experimental(10^{-3}mmol/(mincm2))	7.13	14.53	30.36	49.16	81.39
	Simulated(10^{-3}mmol/(mincm2))	7.20	14.15	29.42	49.78	83.03
	Error (%)	1.09	2.63	3.10	1.24	2.02
0.394V	Experimental(10^{-3}mmol/(mincm2))	3.35	12.02	32.01	52.96	87.50
	Simulated(10^{-3}mmol/(mincm2))	3.25	12.01	34.39	56.58	92.72
	Error (%)	3.08	0.09	7.44	6.84	5.96
0.096V	Experimental(10^{-3}mmol/(mincm2))	1.81	11.95	51.38	89.12	134.13
	Simulated(10^{-3}mmol/(mincm2))	1.77	11.50	45.65	80.06	128.76
	Error (%)	2.38	3.74	11.16	10.18	4.00

Table 4. Error analysis for total methanol crossover with the simulated methanol concentration at the interface for steady states: methanol concentration 0.5-5M; methanol flow rate, 3 $ml\,min^{-1}$, air stoichiometric is greater than 40.

The effects of the cell voltage and methanol feeding concentration on the total methanol crossover and the amount of crossover caused by diffusion and osmosis drag are shown in Table 5 and Figure 10.

feeding Con. (M)		0.5M	1M	2M	3M	5M
crossover V= V_{max}	total (mol/(s*m^2))	1.18×10^{-3}	2.42×10^{-3}	5.08×10^{-3}	8.19×10^{-3}	1.36×10^{-2}
	diffusion percentage	100%	97.37%	96.43%	100%	100%
	drag percentage	0%	2.63%	3.57%	0%	0%
crossover V= 0.394V	total (mol/(s*m^2))	5.69×10^{-4}	1.99×10^{-3}	5.24×10^{-3}	8.84×10^{-3}	1.45×10^{-2}
	diffusion percentage	87.97%	87.42%	88.40%	89.95%	94.91%
	drag percentage	12.03%	12.58%	11.60%	10.05%	5.09%
crossover V= 0.096V	total (mol/(s*m^2))	3.51×10^{-4}	1.96×10^{-3}	8.51×10^{-3}	1.48×10^{-2}	2.23×10^{-2}
	diffusion percentage	74.57%	66.06%	49.92%	50.04%	61.56%
	drag percentage	25.43%	33.94%	50.08%	49.96%	38.44%

Table 5. The effects of the cell voltage and methanol feeding concentration on the total methanol crossover and the percentage of methanol crossover caused by the diffusion and osmosis drag: methanol concentration 0.5-5M; methanol flow rate, 3 ml min^{-1}, air stoichiometric is greater than 40.

The effects of feeding methanol concentration and cell voltage on the percentage of methanol crossover caused by the diffusion and electro-osmosis drag are shown in Figure 11, Figure 12 and Figure 13.

Example 3 **Derivation of the Formula and Explanation of the Method in General**

The first equation is to show the methanol crossover flux j includes two parts, the diffusion part and the electronic drag part. Note that "n" is removed in the second term. This is due to fact that n is always equal to 1.

$$j = -D\frac{\Delta C}{t} + \lambda_m \frac{I}{F} \qquad (3.1)$$

where,

j – methanol cross-over flux

D — the effective diffusivity of the Nafion® electrolyte membrane,

t — the membrane thickness

ΔC – methanol concentration difference between the two sides of the membrane

F — Faraday constant F = 96485 C,

I – current density

λ_m – number of methanol molecules 'dragged" by each proton from the anode to the cathode sides.

Since the methanol concentration on the cathode side is assume to be 0 due to the fast oxidation reaction, we have,

$$j = -D\frac{0 - C_i}{t} + \lambda_m \frac{I}{F}$$

Or,

$$j = D\frac{C_i}{t} + \lambda_m \frac{I}{F} \qquad (3.2)$$

where j can be obtained through the following equation

$$j = \frac{QX}{Av} \qquad (3.3)$$

where,

A— cell active area

Q — cathode total volumetric flow rate

X — CO_2 mole fraction at the cathode exit (%)

v — molar specific volume of CO_2.

Substitute Eq. (3) into the equation (2), we have,

$$\frac{QX}{Av} = D\frac{C_i}{t} + \lambda_m \frac{I}{F}$$

Or,

$$DC_i + \lambda_m I(\frac{t}{nF}) = \frac{QXt}{Av} \qquad (3.4)$$

At any specified current density I and cathode inlet flow rate Q, this equation contains two unknowns, C_i and λ_m. X is the measured valued using a CO_2 sensor at the cathode exit and the rest are all constants.

It is know that at a give current density, C_i and λ_m are uniquely defined, yet it is not possible to determine them since we have two unknowns in one equation. We know that when the current density abruptly changes from one value to another, C_i and λ_m will not change instantaneously. Therefore, if we make two changes of the current density from the same steady-state value (pre-change value) to two different new values (post-change values), we can obtain two equations from Eq. (3.4). In these two equations, the two C_i are equal and the two λ_m are also equal. Now we have two equations with two unknowns. After each change, the current density I used in Eq. (3.4) is the new value (i.e., post change current density) and the X is also the new value, the peak value (transient fuel crossover rate). Basically, using two new current densities and two peak values of the CO_2 concentration, we can uniquely determine the two values of C_i (interface fuel concentration) and λ_m (fuel drag coefficient) at the equilibrium current density – pre-change current density (defined as I_1 in the claims).

Conclusions:

1. The assumption that the methanol concentration at the interface between the anode catalyst layer and the electrolyte membrane does not change simultaneously with the change in cell current or voltage is proved to be a valid assumption.

2. A current as small as $0.002A/cm^2$ in the cell current changes the interface methanol concentration drastically than an open circuit.

3. There exists a linear relationship between methanol drag coefficient and methanol molar fraction at the interface between the anode catalyst layer and electrolyte polymer.

4. The cell voltage or current has no effect on the interface methanol concentration when the methanol feeding concentration is as high as 5M.

5. Methanol crossover decreases at lower voltage when the methanol feeding concentration is low; on the contrary, it increases when methanol feeding concentration is high.

6. For methanol feeding concentration ranges from 0.5 to 5M, when a cell is running at a voltage higher than 0.394V, nearly 90% methanol crossover is caused by the diffusion. Even when the cell voltage is at 0.096V, more than half of the total methanol crossover is caused by the diffusion.

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CLAIMS

We Claim:

1. A method for measuring an interface fuel concentration and a fuel drag coefficient in a fuel cell the method comprising:
   a. measuring a first transient fuel crossover rate and a first post change current density of said fuel cell as said fuel cell transitions from a current density of I_1 to a current density of I_2;
   b. measuring a second transient fuel crossover rate and a second post change current density of said fuel cell as said fuel cell transitions from a current density of I_1 to a current density of I_3; and
   c. determining said interface fuel concentration and said fuel drag coefficient from said first and said second transient fuel crossover rate and said first and said second post change current density;

   wherein I_1, I_2 and I_3 are different from each other.
2. The method of claim 1 wherein said fuel cell comprises an anode catalyst layer, a cathode catalyst layer, and at least one layer of electrolyte.
3. The method of claim 2 wherein said electrolyte is a liquid electrolyte, an electrolyte membrane, or a solid electrolyte.
4. The method of claim 2 wherein said interface fuel concentration is a concentration of fuel between said anode catalyst layer and said electrolyte.
5. The method of claim 1 wherein I_2 is less than I_1 and wherein I_1 is less than I_3.
6. The method of claim 1 wherein said fuel cell comprises an anode diffusion layer, a cathode diffusion layer or both.
7. The method of claim 1 wherein said fuel cell is a liquid fuel cell.
8. The method of claim 1 wherein said fuel cell is selected from the group consisting of polymer electrolyte membrane fuel cell, phosphoric acid fuel cell, direct methanol fuel cell, alkaline fuel cell, solid oxide fuel cell and molten carbonate fuel cell.
9. The method of claim 1 wherein said fuel is a an organic fuel.

10. The method of claim 9 wherein said fuel cell is a direct methanol fuel cell, said organic fuel is methanol, said interface fuel concentration is an interface methanol concentration, and said drag coefficient is a methanol drag coefficient.

11. The method of claim 1 wherein said first transient fuel crossover rate or said second transient fuel crossover rate is determined by measuring a peak value of transient fuel crossover as the fuel crossover rate is decreased, or by measuring a trough value of transient fuel crossover as the fuel crossover rate is increased.

12. The method of claim 1 wherein said first and second transient fuel crossover rate is determined by measuring CO_2 concentration at the cathode side of said fuel cell.

13. The method of claim 1 wherein said fuel cell has the same pressure on an anode side and on a cathode side of said fuel cell.

14. An apparatus for determining an interface fuel concentration or a fuel drag coefficient in a fuel cell, said apparatus comprising:
    a. means for measuring a transient fuel crossover rate in said fuel cell;
    b. means for measuring a current density of said fuel cell;
    c. means for changing a current density of said fuel cell in a stepwise fashion between I_1, and I_3, and between I_2 and I_3.

15. The apparatus of claim 14 further comprising a processor adapted to receive the signals from said means for measuring a transient fuel crossover rate and said means for measuring a current density and to calculate said interface fuel concentration or said fuel drag coefficient.

16. The apparatus of claim 14 wherein said means for measuring a transient fuel crossover rate is a CO_2 detector and a flow meter.

17. The apparatus of claim 14 wherein said means for measuring a current density of said fuel cell is a amp meter, a voltmeter or any electronic device that can measure electric current.

18. The apparatus of claim 14 wherein said means for controlling a current density of said fuel cell is a load bank or a voltage controller.

19. The apparatus of claim 14 wherein said means for changing a current density of said fuel cell is a load bank or a voltage controller.

20. A fuel cell comprising the apparatus of claim 14.

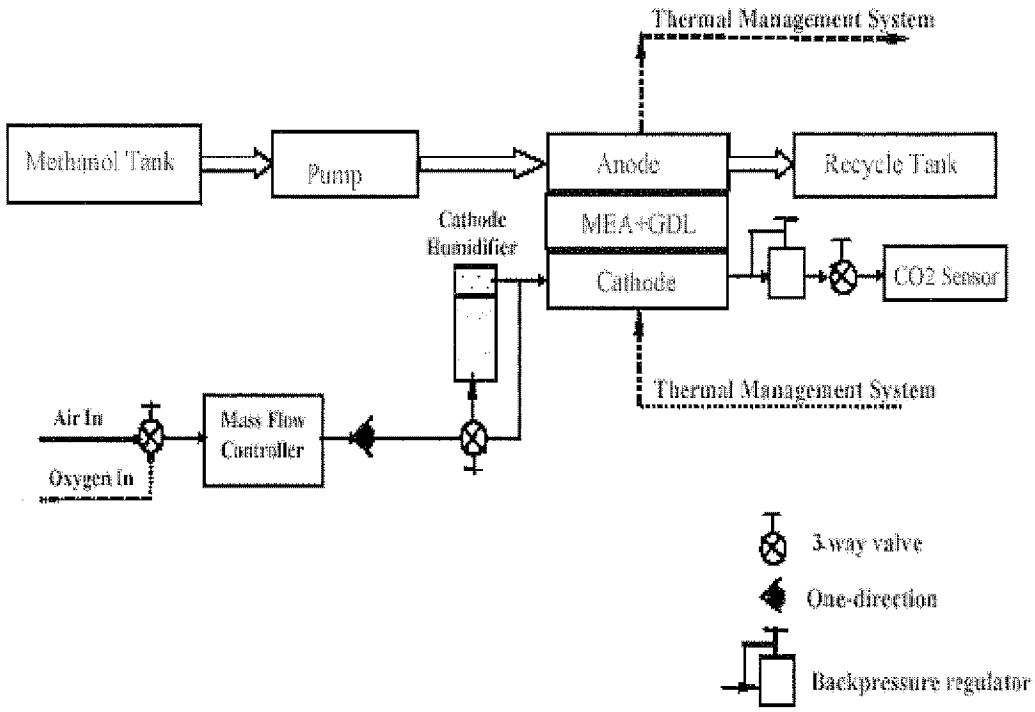


Figure 1.

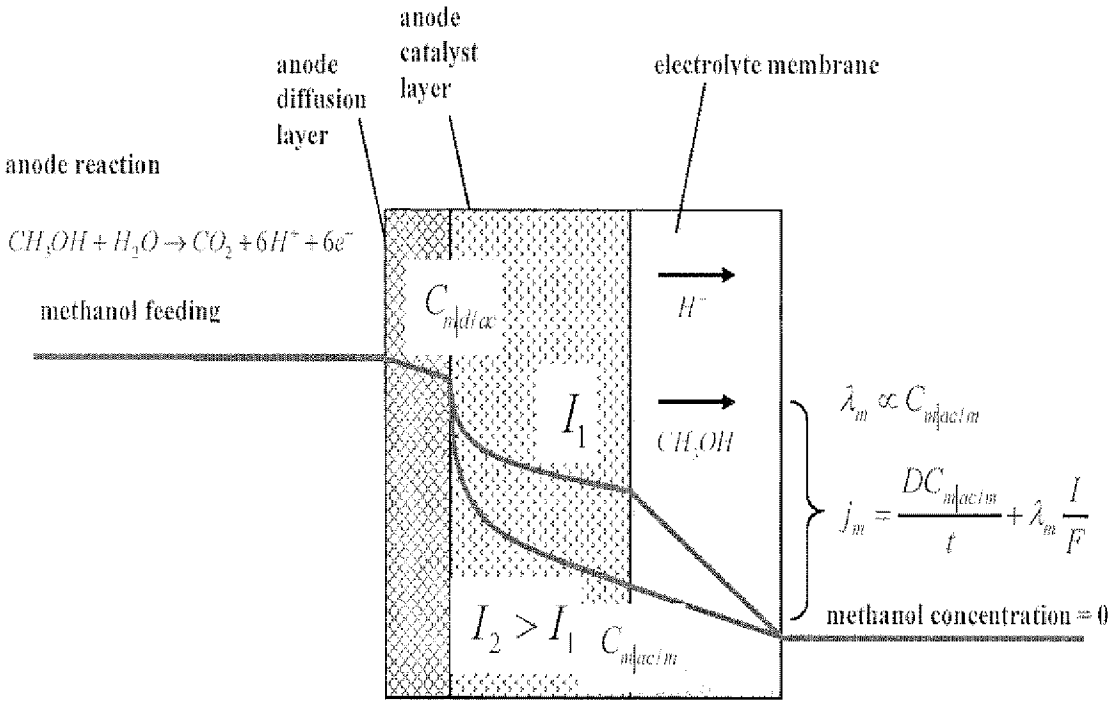


Figure 2.

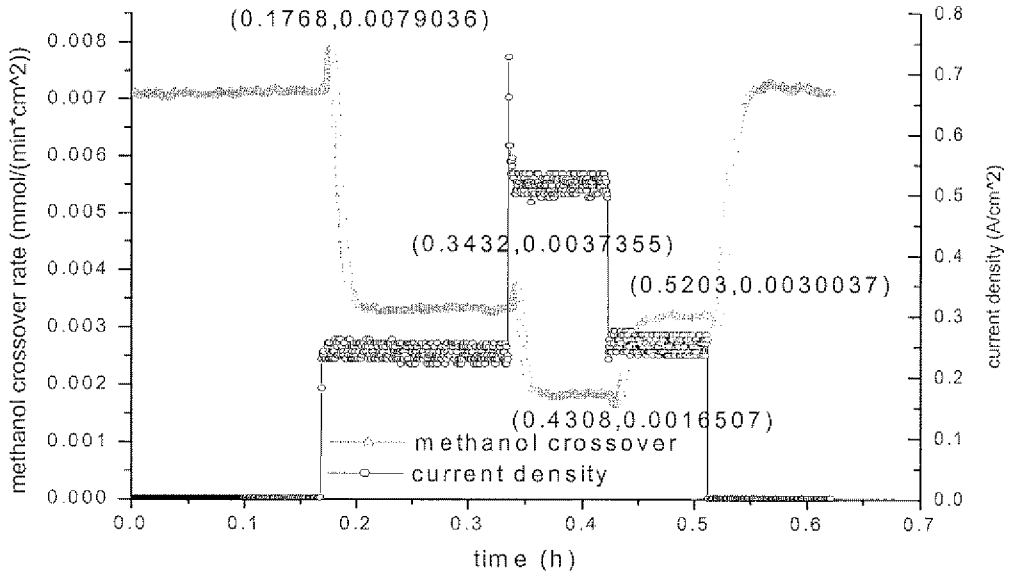


Figure 3.

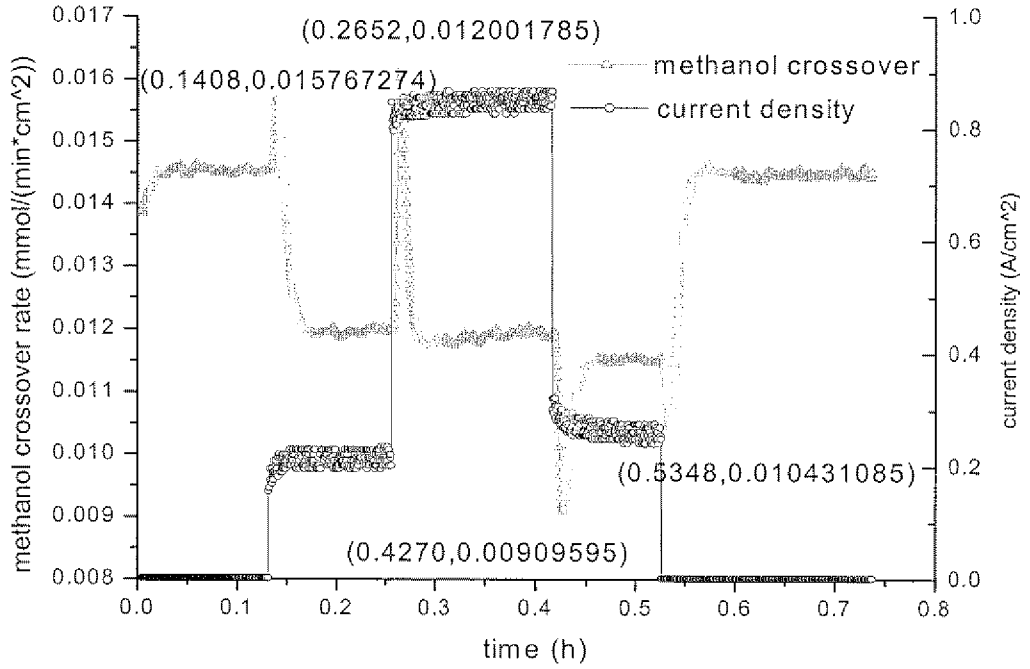


Figure 4.

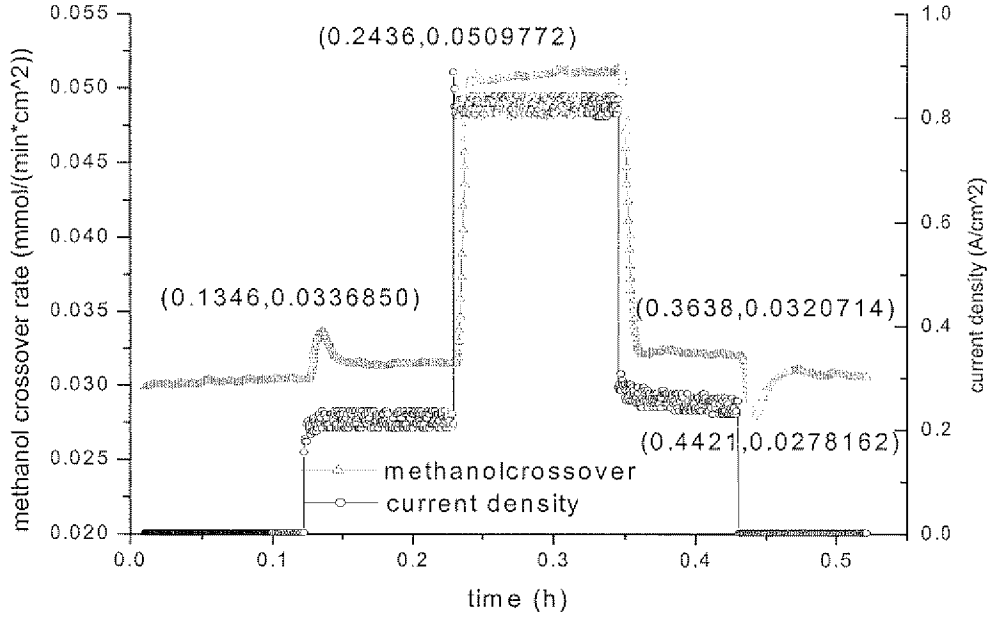
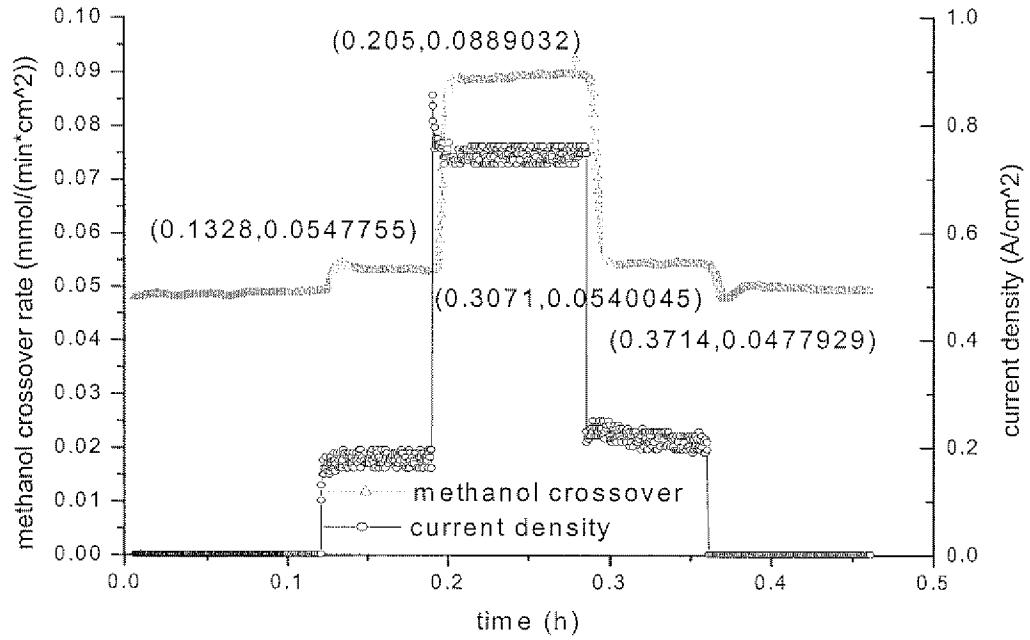


Figure 5.



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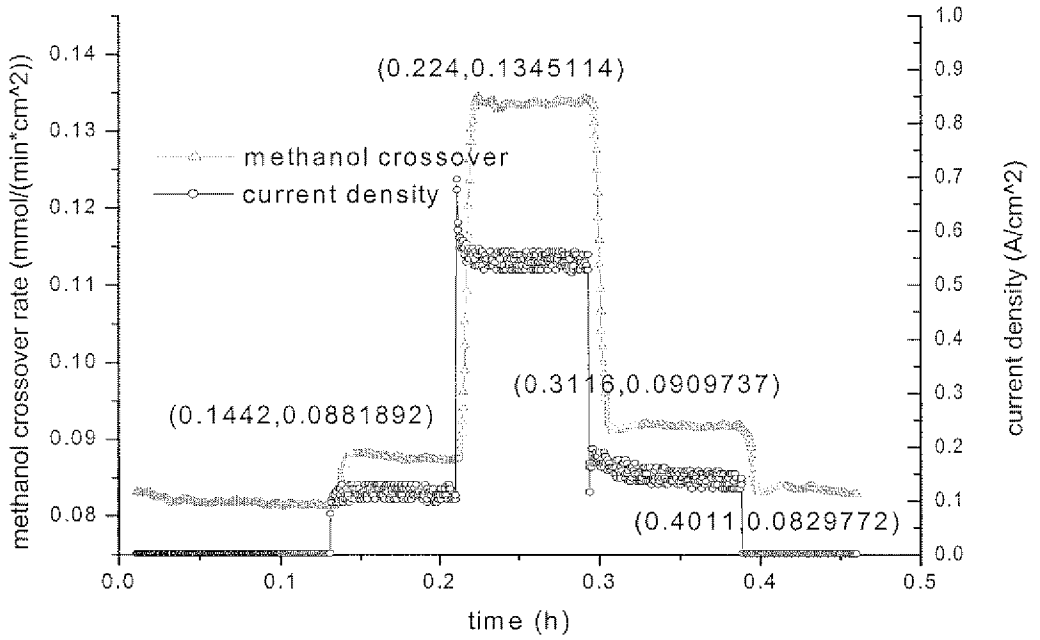

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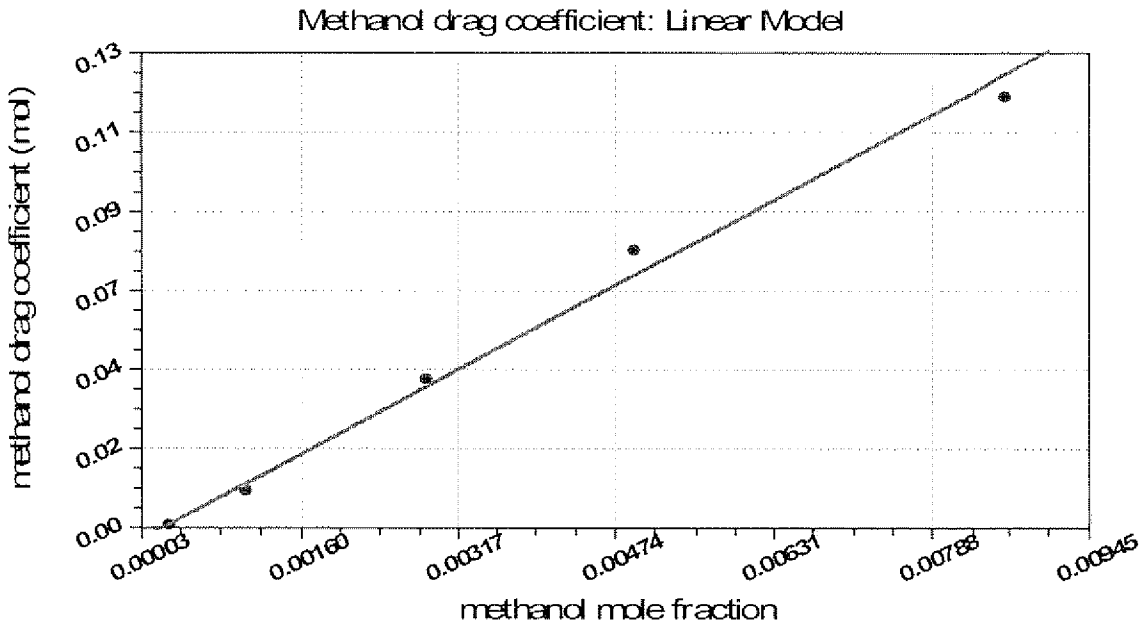

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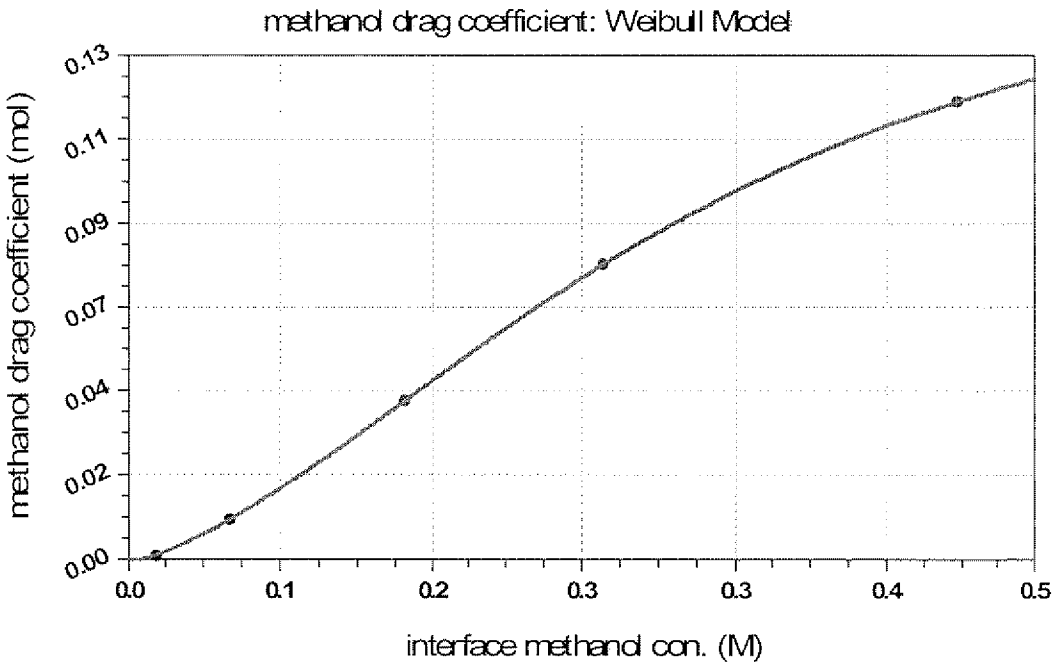

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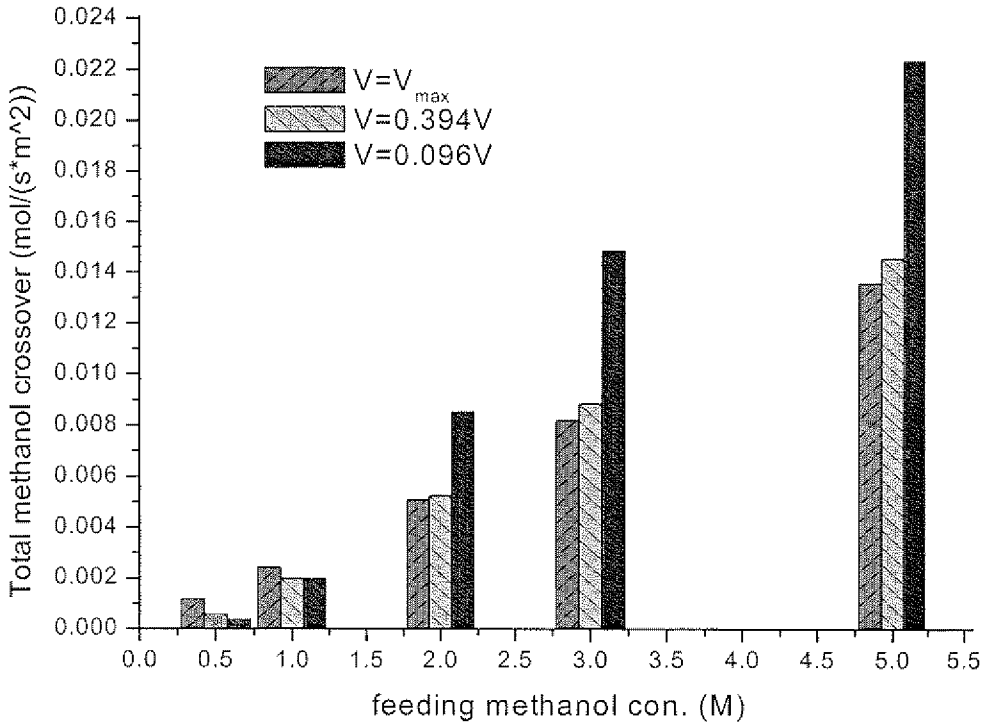

Figure 10.

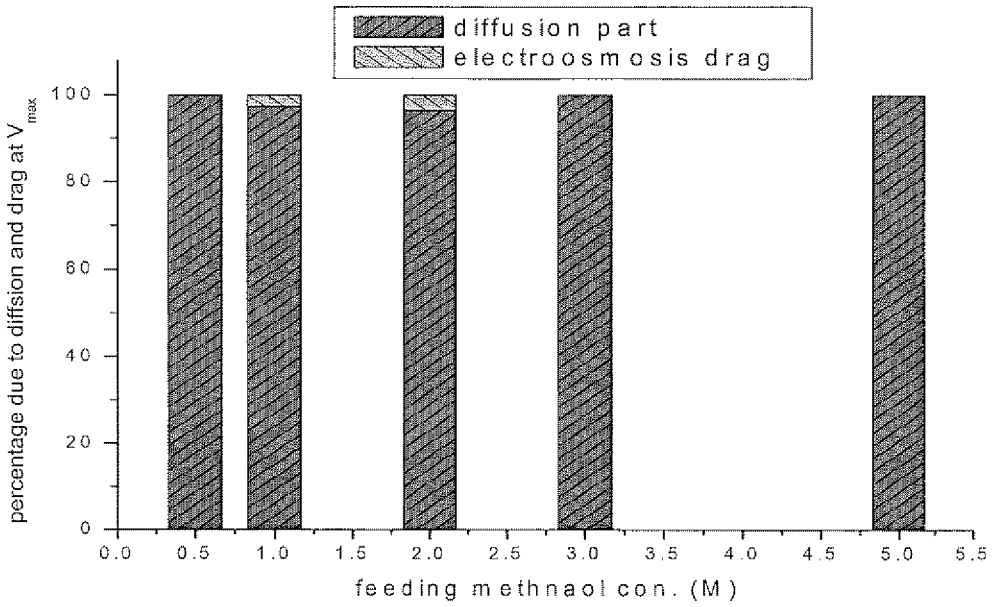

Figure 11.

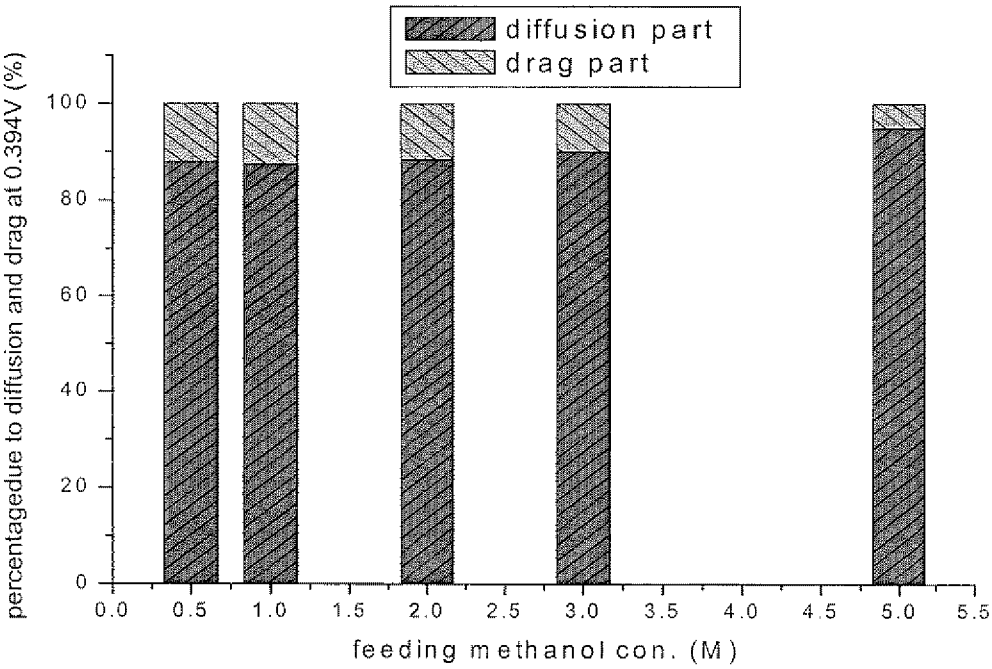

Figure 12.

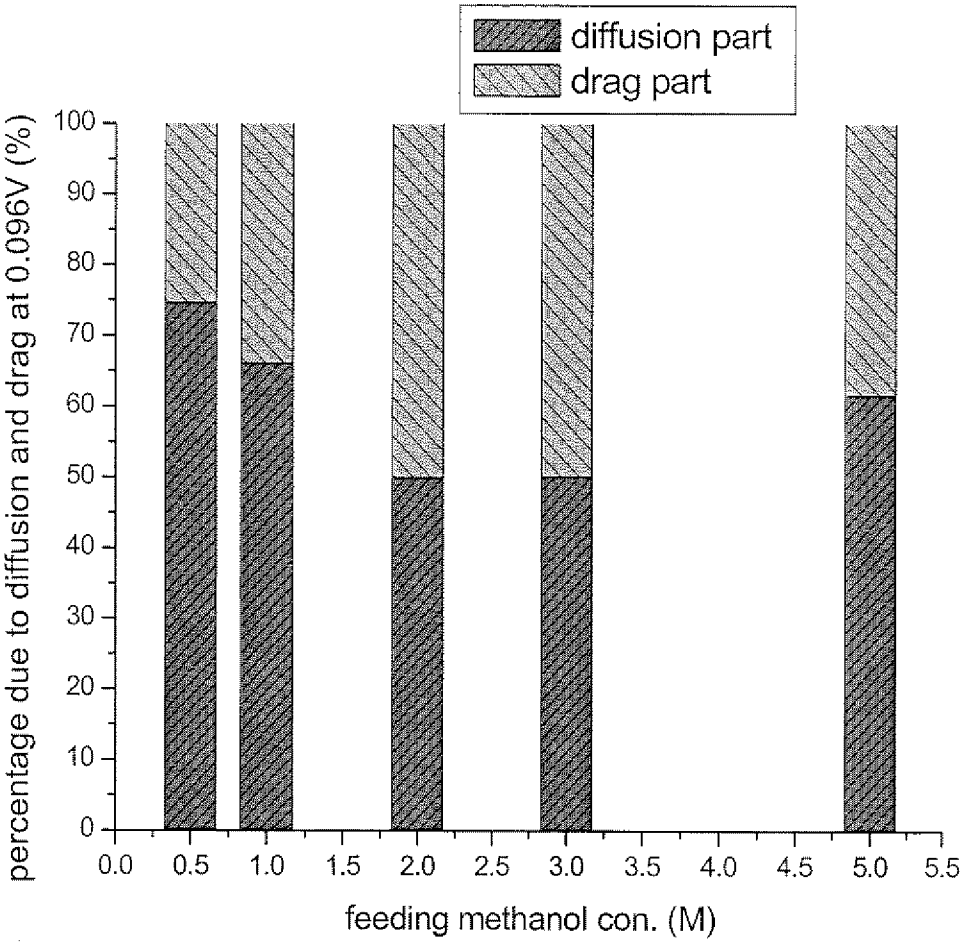
diffusion part
drag part
percentage due to diffusion and drag at 0.096V (%)
0
10
20
30
40
50
60
70
80
90
100
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
feeding methanol con. (M)

Figure 13.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2008/069203

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - H01M 8/10 (2008.04)
USPC - 429/33
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(8) - H01M 8/10 (2008.04)
USPC - 429/33

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6,991,865 B2 (ACKER et al) 31 January 2006 (31.01.2006) *entire document*	1-20
Y	US 2004/0028977 A1 (PICKUP et al) 12 February 2004 (12.02.2004) entire document	1-20
Y	US 6,596,422 B2 (REN) 22 July 2003 (22.07.2003) entire document	1-13
Y	US 6,444,343 B1 (PRAKASH et al) 03 September 2002 (03.09.2002) *entire document*	12, 16

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 September 2008	24 SEP 2008

Name and mailing address of the ISA/US	Authorized officer:
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774