



On the Nature of Mixed Potential in a DMFC

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A 1D + 1D model of a direct methanol fuel cell (DMFC) is developed. Analytical solution for the case of equal oxygen and methanol stoichiometries λ is obtained. The model predicts a new effect: formation of a narrow zone of local current (bridge), which "short-circuits" cell electrodes at vanishingly small current in the load. The bridge arises only under nonzero flux of methanol through the membrane. This effect explains dramatic decrease of DMFC open-circuit voltage known as mixed potential. The expression for voltage loss at open-circuit E_0 is derived; E_0 increases with the rate of crossover and tends to zero with the growth of λ . Numerical estimate for typical cell gives $E_0 \approx 500$ –700 mV, which agrees with the experimental data. The model suggests a method for measuring mean crossover flux through the membrane and indicates conditions for cell operation with zero crossover, regardless of the transport properties of the membrane
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If one connects load to the electrodes of a direct methanol fuel cell (DMFC), already at very small current, cell voltage dramatically drops.^{1–5} Detailed measurements suggest that the effect is caused by methanol permeation through the membrane (methanol crossover).

Typical voltage loss E_0 at open circuit is about 500 mV. In the range of small current densities, this value constitutes the largest portion of the overall voltage loss in DMFCs. The effect thus has been a subject of numerous experimental studies (see *e.g.*, Ref. 6,7 and the literature cited therein).

In spite of extensive studies the origin of the effect still is not fully understood. Possible candidates to explain the value of E_0 include transport of excessive oxygen required to burn methanol on the cathode side,⁸ poisoning of the cathode catalyst by the intermediates of methanol oxidation,⁷ or flooding of the cathode side.^{9,6} Until now, however, there are no reliable estimates in literature, which would enable to confirm or decline the respective conjecture. Recent numerical models of DMFCs^{10,11} also do not explain the nature of E_0 (see Discussion).

In this work we develop a 1D + 1D analytical model of a DMFC which reveals a new effect in DMFC operation. The model predicts formation of a narrow "bridge" of local current, which short-circuits cell electrodes even at small current in the external circuit. The bridge forms only in the presence of crossover; in an ideal cell without crossover the effect does not take place. We derive a formula for the voltage loss due to bridge formation. Numerical estimate shows that this voltage loss agrees with the experimental data on E_0 .

Model

Basic assumptions.—The model is a quasi-2D extension of our 1D DMFC model¹² and thus inherits all assumptions made in Ref. 12 to describe the transport across the cell and kinetics of electrochemical reactions. These assumptions are:

1. The mechanism of methanol and oxygen transport across the respective backing layer is diffusion due to concentration gradient.
2. Transport of methanol through the membrane is due to concentration gradient and electro-osmosis.
3. The variation of oxygen and methanol concentration across the catalyst layer is neglected.
4. Kinetics of methanol oxidation and oxygen reduction obeys the Tafel equation.
5. Permeated methanol is completely consumed in the cathode catalyst layer due to a direct chemical reaction with oxygen.⁸

The discussion of these assumptions is given in Ref. 12.

In this work the model is extended to take into account transport of reactants in the feed channels; the respective assumptions are as follows:

1. We assume plug flow conditions in the channels on both sides of the cell, that is reactant concentrations are uniform across the channel and flow velocity is constant.
2. Pressure in the cathode channel is constant.
3. For simplicity we neglect the effects due to channel curvature and consider a cell equipped with straight channels (Fig. 1).

Continuity equations in the feed channels.—The z axis is directed along the channel (Fig. 1). Methanol and oxygen mass balance equations in the channels are

$$h^a v^a c^a \frac{\partial \psi}{\partial z} = - \frac{j}{6F} - N_{\text{cross}} \quad [1]$$

$$h^c v^c c^c \frac{\partial \xi}{\partial z} = - \frac{j}{4F} - \frac{3}{2} N_{\text{cross}} \quad [2]$$

where the superscripts "a" and "c" refer to the anode and the cathode side respectively, h is channel height, v is flow velocity, c is total molar concentration of the mixture in the channel, $\psi(z)$ and $\xi(z)$ are molar fractions of methanol and oxygen, respectively, $j(z)$ is local current density

$$N_{\text{cross}} = \frac{j_{\text{lim}}^a}{6F} \left(\frac{\beta}{1 + \beta} \right) \left(1 - \frac{j}{j_{\text{lim}}^a} \right) \quad [3]$$

is molar flux of methanol through the membrane (crossover flux),¹² $j_{\text{lim}}^a = 6FD_b^a c^a \psi / l_b^a$ is local limiting current density due to methanol transport through the backing layer, and β is a ratio of methanol mass-transfer coefficients in the membrane and in the anode backing layer

$$\beta = \frac{D_m l_b^a}{D_b^a l_m} \quad [4]$$

Here D_m and D_b^a are diffusion coefficients of methanol in the membrane and in the anode backing layer, respectively, l_b^a and l_m are backing layer and membrane thickness, respectively.

The expression for N_{cross} was obtained in Ref. 12 from the balance of methanol fluxes in the anode backing layer and in the membrane. Further analysis has shown that for typical methanol concentrations (0.5–2 M) the terms which describe methanol drag through the membrane can be neglected. The dominating mechanism of crossover is thus diffusion due to the concentration

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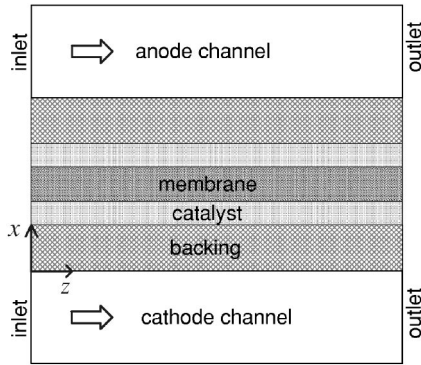


Figure 1. Sketch of the cell and the system of coordinates.

gradient.¹² The resulting N_{cross} (Eq. 3) linearly decreases with the current density j . This behavior correlates with the experimental observations.^{5,13,14}

It is convenient to introduce dimensionless variables

$$\tilde{j} = \frac{j}{j_{\text{lim}}^a}, \quad \tilde{J} = \frac{J}{j_{\text{lim}}^a}, \quad \tilde{z} = \frac{z}{L}, \quad \tilde{\psi} = \frac{\psi}{\psi^0}, \quad \tilde{\xi} = \frac{\xi}{\xi^0} \quad [5]$$

where L is channel length

$$j_{\text{lim}}^a = \frac{6FD_b^a c^a \psi^0}{l_b^a} \quad [6]$$

and the superscript “0” indicates the values at the channel inlet (at $\tilde{z} = 0$). DMFC is usually run at constant oxygen and methanol stoichiometries λ^a and λ^c , respectively. By definition

$$\lambda^a = \frac{6Fh^a v^a c^a \psi^0}{LJ}, \quad \lambda^c = \frac{4Fh^c v^c c^c \xi^0}{LJ}$$

where J is mean current density in a cell.

Using these relations, 1 and 2 transform to

$$\lambda^a \tilde{J} \frac{\partial \tilde{\psi}}{\partial \tilde{z}} = -(\tilde{J} + \tilde{j}_{\text{cross}}) \quad [7]$$

$$\lambda^c \tilde{J} \frac{\partial \tilde{\xi}}{\partial \tilde{z}} = -(\tilde{J} + \tilde{j}_{\text{cross}}) \quad [8]$$

where

$$\tilde{j}_{\text{cross}} = \frac{6FN_{\text{cross}}}{j_{\text{lim}}^a} = \beta_1 \tilde{\psi} \left(1 - \frac{\tilde{J}}{\tilde{\psi}} \right) \quad [9]$$

is equivalent crossover current density. Here

$$\beta_1 = \frac{\beta}{1 + \beta} \quad [10]$$

With Eq. 9, Eq. 7 and 8 take a form

$$\lambda^a \tilde{J} \frac{\partial \tilde{\psi}}{\partial \tilde{z}} = -[\tilde{J} + \beta_1(\tilde{\psi} - \tilde{j})] \quad [11]$$

$$\lambda^c \tilde{J} \frac{\partial \tilde{\xi}}{\partial \tilde{z}} = -(\tilde{J} + \beta_1(\tilde{\psi} - \tilde{j})) \quad [12]$$

Polarization voltages.—Polarization voltages η^a, η^c of the anode and the cathode sides, respectively, are¹²

$$\frac{\eta^a}{b^a} = \ln\left(\frac{j}{k^a}\right) - \ln\left(1 - \frac{j}{j_{\text{lim}}^a}\right) + \ln(1 + \beta) \quad [13]$$

$$\frac{\eta^c}{b^c} = \ln\left(\frac{j}{k^c}\right) - \ln\left(1 - \frac{j + j_{\text{cross}}}{j_{\text{lim}}^c}\right) \quad [14]$$

Here b is Tafel slope

$$k^a = l_t^a i_*^a \frac{c^a \psi}{c_{\text{ref}}^a}, \quad k^c = l_t^c i_*^c \frac{c^c \xi}{c_{\text{ref}}^c} \quad [15]$$

l_t is catalyst layer thickness, i_* is exchange current density per unit volume, c_{ref} is reference molar concentration, and

$$j_{\text{lim}}^c = 4F \frac{D_b^c c^c \xi}{l_b^c} \quad [16]$$

is local limiting current density due to oxygen transport through the backing layer, D_b^c is oxygen diffusion coefficient in the cathode backing layer.

The first terms on the right side of Eq. 13 and 14 describe reaction activation potentials. The second term in Eq. 13 describes voltage loss due to methanol transport through the backing layer; the third term in this equation represents anodic voltage loss due to methanol leakage through the membrane.

The second term on the right side of Eq. 14 describes the net voltage loss due to oxygen transport through the backing layer. This term takes into account transport of oxygen, required for the electrochemical reaction and transport of excessive oxygen, required to burn permeated methanol (the term \tilde{j}_{cross}).

Equations 13 and 14 are not empirical relations. These equations are exact solutions of the problem of DMFC performance in 1D approximation. Equations 13 and 14 are valid when

$$j \ll \min\{j_*^a, j_*^c\}$$

where $j_* = 2\sigma_t b / l_t$ is characteristic current density, and σ_t is proton conductivity of the respective catalyst layer. This work is focused mainly on cell operation at small currents; we thus may safely assume that this inequality is fulfilled.

Using dimensionless variables (Eq. 5), Eq. 13 and 14 take a form

$$\frac{\eta^a}{b^a} = \ln\left(\frac{\tilde{j}}{q\tilde{\psi}}\right) - \ln\left(1 - \frac{\tilde{j}}{\tilde{\psi}}\right) + \ln(1 + \beta) \quad [17]$$

$$\frac{\eta^c}{b^c} = \ln\left(\frac{\tilde{j}}{\alpha q \tilde{\xi}}\right) - \ln\left(1 - \frac{\tilde{j} + \tilde{j}_{\text{cross}}}{\gamma \tilde{\xi}}\right) \quad [18]$$

where

$$q = \frac{l_t^a i_*^a l_b^a}{6FD_b^a c_{\text{ref}}^a}, \quad \alpha = \frac{l_t^c i_*^c c_{\text{ref}}^a}{l_t^a i_*^a c_{\text{ref}}^c} \left(\frac{c^c \xi^0}{c^a \psi^0} \right), \quad \gamma = \frac{2D_b^c l_b^a}{3D_b^a l_b^c} \left(\frac{c^c \xi^0}{c^a \psi^0} \right)$$

are dimensionless parameters and \tilde{j}_{cross} is given by Eq. 9.

Cell voltage is

$$V_{\text{cell}} = V_{\text{oc}} - \eta_a - \eta_c - R_n J \quad [19]$$

where V_{oc} is thermodynamic open-circuit voltage (OCV) and R_n is contact resistance. Fuel cell electrodes are equipotential, that is the sum

$$E = \eta^a(\tilde{z}) + \eta^c(\tilde{z}) \quad [20]$$

does not depend on \tilde{z} . Introducing dimensionless potentials

$$\tilde{\eta} = \frac{\eta}{b^a}, \quad \tilde{E} = \frac{E}{b^a} \quad [21]$$

Eq. 20 takes a form $\tilde{\eta}^a + \tilde{\eta}^c = \tilde{E}$. With Eq. 17 and 18 we finally obtain

$$\ln\left(\frac{\tilde{j}}{q\tilde{\psi}}\right) - \ln\left(1 - \frac{\tilde{j}}{\tilde{\psi}}\right) + \ln(1 + \beta) + p \left[\ln\left(\frac{\tilde{j}}{\alpha q \tilde{\xi}}\right) - \ln\left(1 - \frac{\tilde{j} + \tilde{j}_{\text{cross}}}{\gamma \tilde{\xi}}\right) \right] = \tilde{E} \quad [22]$$

where

$$p = \frac{b^c}{b^a} \quad [23]$$

is a ratio of Tafel slopes. Note that the anodic Tafel slope b^a is used to normalize potentials.

Equations 11, 12, and 22 form a system of 3 equations for 3 unknowns: $\tilde{\psi}(\tilde{z})$, $\tilde{\xi}(\tilde{z})$, and $\tilde{j}(\tilde{z})$. This is a 1D + 1D model of DMFC: the relation of local current density and voltage loss (Eq. 22) couples two equations, Eq. 11 and 12, for methanol and oxygen concentrations in the respective channel.

Numerical and asymptotic analysis of this system is given in Ref. 15. In this paper we analyze the case of equal oxygen and methanol stoichiometries, when the system discussed has exact analytical solution.

The Case of $\lambda^a = \lambda^c$: Exact Solution

Along-the-channel profiles.—If $\lambda^a = \lambda^c$ solution to the system discussed is

$$\tilde{\psi} = \tilde{\xi}, \quad \tilde{j} = \kappa \tilde{\psi} \quad [24]$$

Indeed, under $\lambda^a = \lambda^c = \lambda$ Eq. 11 and 12 coincide, that is $\tilde{\psi} = \tilde{\xi}$. Substituting $\tilde{j} = \kappa \tilde{\psi}$ into Eq. 11 we get

$$\lambda \tilde{j} \frac{\partial \tilde{\psi}}{\partial \tilde{z}} = -[\kappa + \beta_1(1 - \kappa)] \tilde{\psi} \quad [25]$$

Solving this equation and taking into account Eq. 24 we find

$$\tilde{\xi} = \tilde{\psi} = \exp\left(-\frac{\tilde{z}}{\mu}\right) \quad [26]$$

where μ is the characteristic length

$$\mu = \frac{\lambda \tilde{j}}{\kappa + \beta_1(1 - \kappa)} \quad [27]$$

From Eq. 24 we find

$$\tilde{j} = \kappa \exp\left(-\frac{\tilde{z}}{\mu}\right) \quad [28]$$

Parameter κ hence is local current density at the inlet: $\kappa = \tilde{j}(0)$. Substituting Eq. 26 and $\tilde{j} = \kappa \tilde{\psi}$ into Eq. 9 we get

$$\tilde{j}_{\text{cross}} = \beta_1(1 - \kappa) \exp\left(-\frac{\tilde{z}}{\mu}\right) \quad [29]$$

All variables thus decrease exponentially along \tilde{z} with the same characteristic scale (Eq. 27). Note that the exponential-like decay of local current density with \tilde{z} was obtained in fully 2D numerical calculations of Birgersson *et al.*¹⁶

Substituting $\tilde{j} = \kappa \tilde{\psi}$ into Eq. 17 and $\tilde{j} = \kappa \tilde{\xi}$ into Eq. 18 we find

$$\frac{\eta^a}{b^a} = \ln\left(\frac{\kappa}{q}\right) - \ln(1 - \kappa) + \ln(1 + \beta) \quad [30]$$

$$\frac{\eta^c}{b^c} = \ln\left(\frac{\kappa}{\alpha q}\right) - \ln\left(1 - \frac{\kappa + \beta_1(1 - \kappa)}{\gamma}\right) \quad [31]$$

We see that polarization voltages on both sides of the cell are constant along \tilde{z} . Parameter κ is obtained from the condition $\int_0^1 \tilde{j} d\tilde{z}$

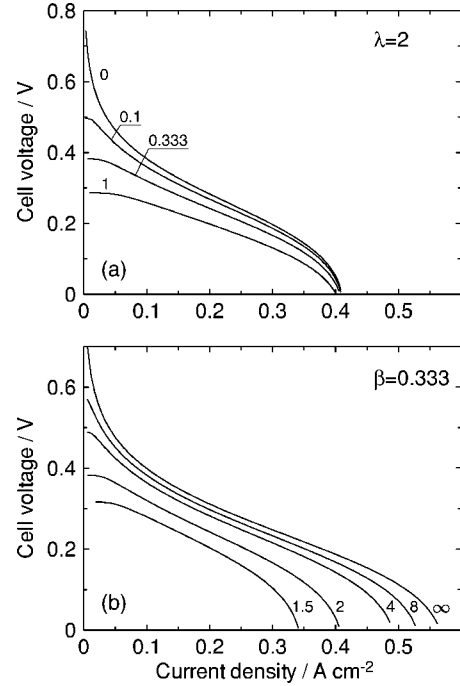


Figure 2. Voltage current curves of DMFC with equal stoichiometries of methanol and oxygen. (a) $\lambda = 2$; indicated are the values of crossover parameter β . (b) $\beta = 0.333$; indicated are the values of λ . Parameters used for calculations are given in Table I.

$= \tilde{j}$. Using here $\tilde{j} = \kappa \exp(-\tilde{z}/\mu)$ and calculating the integral we find $\kappa \mu [1 - \exp(-1/\mu)] = \tilde{j}$. With Eq. 27, after simple manipulations we get the following equation for κ

$$\frac{\kappa + \beta_1(1 - \kappa)}{\lambda \ln\left(1 - \frac{\kappa + \beta_1(1 - \kappa)}{\kappa \lambda}\right)} = -\tilde{j} \quad [32]$$

Equations 19 and 30-32 determine the cell polarization curve. For a given \tilde{j} , β , and λ solution to Eq. 32 gives κ . Equations 30 and 31 then give η^a and η^c ; cell voltage is calculated from Eq. 19.

Cell polarization curves for several values of β and λ are shown in Fig. 2. The other parameters are listed in Table I. The increase in β reduces OCV (Fig. 2a). Furthermore, for a given β voltage loss at open circuit E_0 decreases with the growth of λ (Fig. 2b). At $\lambda \rightarrow \infty$ OCV reaches the value $V_{oc} - E_0|_{\lambda \rightarrow \infty}$, where $E_0|_{\lambda \rightarrow \infty} \approx 100$ mV (see the following). The effect of lowering cell OCV is well known in DMFC studies; the above-described model explains the physics of this effect.

Table I. Parameters used in calculations.

	Anode	Cathode
Temperature (°C)	70	70
Pressure (atm)	2	2
D_b (cm ² s ⁻¹)	2×10^{-5}	3×10^{-3}
i^* (A cm ⁻³)	10^{-2}	1
c_{ref} (mol cm ⁻²)	10^{-3}	7×10^{-5}
Oxygen molar fraction ξ^0	--	0.2
Methanol molar fraction ψ^0	0.018 (1 M)	--
Tafel slope b (V)	0.05	0.05
Catalyst layer thickness l_t (cm)	10^{-3}	10^{-3}
Backing layer thickness l_b (cm)	2×10^{-2}	2×10^{-2}
Membrane thickness l_m (cm)	10^{-2}	
D_m for $\beta = 0.1, 0.333, 1.0$ (cm ² s ⁻¹)	$10^{-6}, 3.33 \times 10^{-6}, 10^{-5}$	

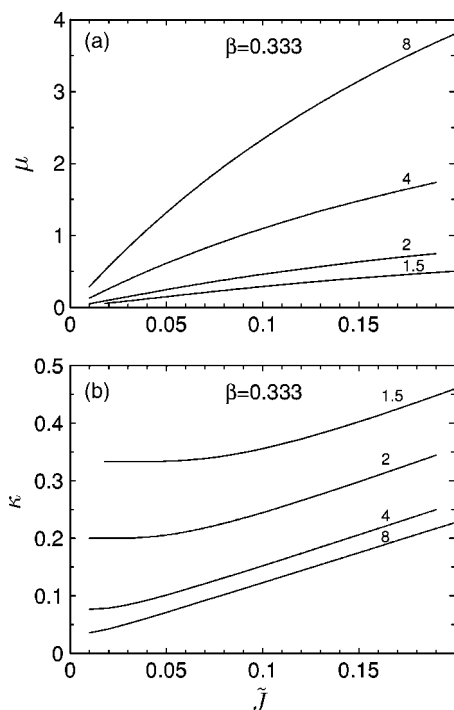


Figure 3. Characteristic scale of the exponent μ and local current density at the inlet κ in Eq. 28 as a function of dimensionless mean current density \tilde{J} for indicated values of λ . Crossover parameter $\beta = 0.333$; the other parameters are given in Table I.

Depolarization at zero current: mixed potential.—Analytical solutions of the previous section give exponential decrease of $\tilde{\psi}$, $\tilde{\xi}$, \tilde{j} , and \tilde{j}_{cross} with \tilde{z} and constant overpotentials η^a, η^c . The function $\tilde{j}(\tilde{z})$ (Eq. 28) is of the most interest, because parameter κ determines overpotentials (Eq. 30 and 31).

Parameter κ is the solution to Eq. 32; μ in Eq. 28 is given by Eq. 27. Both κ and μ depend on \tilde{J} ; behavior of κ and μ as $\tilde{J} \rightarrow 0$ determines cell voltage at zero current. To rationalize this behavior consider first the limiting cases.

In case of zero crossover we put $\beta_1 = 0$ and Eq. 32 gives

$$\kappa = -\tilde{J}\lambda \ln\left(1 - \frac{1}{\lambda}\right) \quad [33]$$

The characteristic scale μ (Eq. 27) then reduces to

$$\mu = -\left[\ln\left(1 - \frac{1}{\lambda}\right)\right]^{-1} \quad [34]$$

We see that as mean current density tends to zero, the “amplitude” κ of local current density (Eq. 28) also tends to zero, whereas μ does not change. If, therefore, an ideal cell (without crossover) is run at a constant $\lambda^a = \lambda^c = \lambda$, the shape of local current density along \tilde{z} is the same for all points of cell polarization curve. The variation of \tilde{J} simply rescales the whole curve $\tilde{j}(\tilde{z})$.

Crossover, however, adds additional degree of freedom. If $\beta_1 \neq 0$, the characteristic scale of exponent μ varies with \tilde{J} . This can be shown explicitly for the case of large λ : the logarithm in Eq. 32 then can be expanded and we get $\kappa = \tilde{J}$. With this κ Eq. 27 yields

$$\mu = \frac{\tilde{J}\lambda}{\tilde{J} + \beta_1(1 - \tilde{J})} \quad [35]$$

We see that now $\mu \rightarrow 0$ as $\tilde{J} \rightarrow 0$. Therefore, as mean current

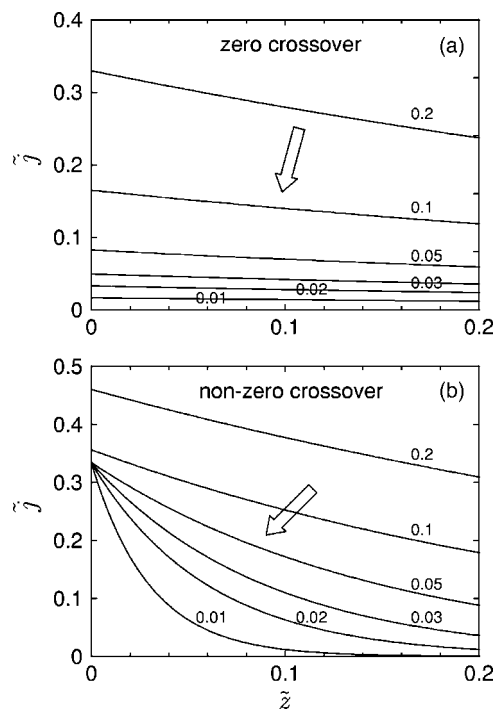


Figure 4. The shape of local current density along the channel for indicated values of dimensionless mean current density \tilde{J} in a cell. (a) The case of zero crossover ($\beta = 0$) and (b) nonzero crossover ($\beta = 0.333$). In both cases $\lambda = 1.5$; the other parameters are given in Table I. Arrows indicate evolution of the curve as $\tilde{J} \rightarrow 0$.

density tends to zero, both κ and μ in Eq. 28 tend to zero. Thus, at small \tilde{J} local current \tilde{j} decreases with \tilde{z} faster than at large \tilde{J} .

Most interesting is the case of finite λ . Numerical solution to Eq. 32 for various λ is shown in Fig. 3. As $\tilde{J} \rightarrow 0$ we have again $\mu \rightarrow 0$, whereas κ now tends to nonzero value κ_0 (Fig. 3), which is solution to Eq. 32 with $\tilde{J} = 0$. Clearly, as $\tilde{J} \rightarrow 0$ the expression under the logarithm in Eq. 32 should tend to zero. For κ_0 we thus have an equation

$$1 - \frac{\kappa_0 + \beta_1(1 - \kappa_0)}{\kappa_0\lambda} = 0$$

The solution is

$$\kappa_0 = \frac{\beta_1}{\lambda - 1 + \beta_1} = \frac{\beta}{\lambda(1 + \beta) - 1} \quad [36]$$

With $\kappa = \kappa_0$ Eq. 27 gives

$$\mu = \frac{\lambda(\lambda(1 + \beta) - 1)\tilde{J}}{\beta(1 + \lambda)} \quad [37]$$

which vanishes as $\tilde{J} \rightarrow 0$. Therefore, as $\tilde{J} \rightarrow 0$ near the inlet forms a narrow “bridge” of local current with nonzero amplitude κ_0 . The width of the bridge μ decreases with \tilde{J} .

This is illustrated in Fig. 4. In case of zero crossover κ (Eq. 33) decreases linearly with \tilde{J} , whereas μ (Eq. 34) remains constant (Fig. 4a). Local current “dies out” uniformly over the cell surface; in the logarithmic scale the curves in Fig. 4a are parallel straight lines.

In case of nonzero crossover μ (Eq. 37) tends to zero with \tilde{J} , whereas κ tends to a constant value κ_0 (Eq. 36, Fig. 4b). An important point is that the mean current density in the bridge \tilde{j}_b remains finite as total current in the system tends to zero. Indeed, $\tilde{j}_b \approx (1/\mu) \int_0^1 \kappa_0 \exp(-\tilde{z}/\mu) d\tilde{z} = \kappa_0[1 - \exp(-1/\mu)]$. Because μ

Table II. Voltage loss at open circuit for indicated values of β and λ .

β	0.1	0.333	1.0
$E_0 _{\lambda=8}$ (mV)	520	637	738
$E_0 _{\lambda=\infty}$ (mV)	13	43	135

$\rightarrow 0$ as $\tilde{J} \rightarrow 0$, we have $\tilde{j}_b \rightarrow \kappa_0$. Eq. 36, therefore, gives the dependence of local current density in the bridge on crossover parameter β and stoichiometry λ . Physically, β (Eq. 4) is a ratio of mass-transfer coefficients of methanol in the membrane and in the backing layer. Fast diffusion of methanol through the membrane or slow methanol transport through the anode backing layer increase β .

Overpotentials (Eq. 13 and 14) depend on the local current density, rather than on the total current in the system. Formation of the bridge with finite current density thus induces finite overpotentials on both sides of the cell. The voltage loss induced by the bridge is a sum $E_0 = \eta^a + \eta^c$ calculated with $\kappa = \kappa_0$. Using here Eq. 30 and 31 we get

$$E_0 = b^a \left[\ln\left(\frac{\kappa_0}{q}\right) - \ln(1 - \kappa_0) + \ln(1 + \beta) \right] + b^c \left[\ln\left(\frac{\kappa_0}{\alpha q}\right) - \ln\left(1 - \frac{\kappa_0 + \beta_1(1 - \kappa_0)}{\gamma}\right) \right] \quad [38]$$

where κ_0 is given by Eq. 36.

With the parameters in Table I and $\lambda = 8$ we find the values shown in the second row of Table II. Thermodynamic OCV of DMFC is about 1.2 V. The bridge thus reduces cell OCV to 0.5- 0.7 V, which agrees with the experiments.^{1,3,5}

OCV decreases as soon as the cell is connected to any load resistance. The bridge forms already at very small (strictly speaking, at infinitesimal) total current in the load. Physically, the bridge arises due to the lack of oxygen in the cell. At a certain distance from the inlet of the cathode channel most of the available oxygen is consumed in the reaction with permeated methanol. The amount of oxygen available for current generation is limited there and this induces "contraction" of local current into a bridge. The bridge thus arises regardless of the details of kinetics of electrochemical reactions; its nature is determined mainly by electrostatic and transport phenomena.

According to Eq. 36, κ_0 tends to zero as $\lambda \rightarrow \infty$. The voltage loss at open circuit E_0 can, therefore, be effectively reduced, increasing λ at small currents (Fig. 2b). Physically, the increase in λ increases the characteristic size μ (Eq. 37, Fig. 3a), thus "smearing out" the bridge over the larger surface.^a

The limit of large λ : one-dimensional cell.—If $\lambda \gg 1 + \beta_1(1/\kappa - 1)$, the logarithm in Eq. 32 can be expanded and we get $\kappa = \tilde{J}$. Substituting $\kappa = \tilde{J}$ into Eq. 30 and 31 and using the resulting expressions to calculate voltage loss $E_0 = \eta^a + \eta^c$, we find

$$E_0 = b^a \left[\ln\left(\frac{\tilde{J}}{q}\right) - \ln(1 - \tilde{J}) + \ln(1 + \beta) \right] + b^c \left[\ln\left(\frac{\tilde{J}}{\alpha q}\right) - \ln\left(1 - \frac{\tilde{J} + \beta_1(1 - \tilde{J})}{\gamma}\right) \right] \quad [39]$$

Eq. 39 is voltage loss, obtained in Ref. 12 within the scope of the 1D DMFC model. Clearly, in the case of large λ the along-the-channel variation of all parameters is small and we come to the formula for a one-dimensional cell.

In this limit the bridge does not form and E_0 is given by nonvanishing terms in Eq. 39 as $\tilde{J} \rightarrow 0$. However, one has to be careful when passing to the limit $\tilde{J} \rightarrow 0$ in Eq. 39. The formal limit cannot be calculated because the activation terms in Eq. 39 originate from the Tafel equation, which is not valid in the limit of $\tilde{J} \rightarrow 0$. Physically, at small currents the Tafel equation should be replaced with the Bultler-Volmer formula, which gives zero activation voltage at zero current density.^b

To pass to the limit $\tilde{J} \rightarrow 0$ in Eq. 39 we thus have to drop out activation terms $\ln(\tilde{J}/q), \ln[\tilde{J}/(\alpha q)]$ and put $\tilde{J} = 0$ in the other terms. This gives

$$E_0|_{\lambda=\infty} = b^a \ln(1 + \beta) - b^c \ln\left(1 - \frac{\beta}{(1 + \beta)\gamma}\right) \quad [40]$$

With the parameters from Table I we get the values $E_0|_{\lambda=\infty}$ shown in the third row of Table II. For all β "1D values" $E_0|_{\lambda=\infty}$ are significantly smaller than $E_0|_{\lambda=8}$. Thus, the effect of mixed potential cannot be explained within the scope of the 1D DMFC model (see also the Discussion section).

Cross-linked feeding.—Consider cell operation at the oxygen-limiting current density. Formally, operation at the limiting current density is equivalent to infinite voltage loss \tilde{E} . The expression under the last logarithm on the left side of Eq. 22 should tend to zero and we get $\tilde{j} + \tilde{j}_{\text{cross}} = \gamma\tilde{\xi}$, or $\tilde{j} + \beta_1(\tilde{\psi} - \tilde{j}) = \gamma\tilde{\xi}$. Using here $\tilde{j} = \kappa\tilde{\psi}$ (Eq. 24) we find

$$\kappa + \beta_1(1 - \kappa) = \gamma$$

If $\gamma = 1$ we get $\kappa = 1$ and thus $\tilde{j}_{\text{cross}} = \beta_1(1 - \kappa)\tilde{\psi} = 0$, regardless of β_1 for any z . This case is of particular interest.

$\gamma = 1$ is equivalent to $j_{\text{lim}}^a = j_{\text{lim}}^c$, or $6FD_b^a c_M^0 / l_b^a = 4FD_b^c c_{\text{ox}}^0 / l_b^c$. Physically, $\gamma = 1$ means that at the inlet the flux of oxygen across the cathode backing layer equals the flux of methanol across the anode backing layer. Both fluxes are maximal because they provide the limiting current density. The concentrations of oxygen and methanol in the respective catalyst layer thus tend to zero.

The fact that $\tilde{j}_{\text{cross}} = 0$ independent of z means that the equality of oxygen and methanol transverse fluxes at $\tilde{z} = 0$ provides their equality at any \tilde{z} . The condition

$$\lambda^a = \lambda^c \text{ and } j_{\text{lim}}^a = j_{\text{lim}}^c \quad [41]$$

thus describes the regime of *cross-linked feeding*: everywhere along the channels available methanol and oxygen are consumed, so that regardless of β crossover is exactly zero and one does not need the membrane.

In this regime $\kappa = 1$ and the characteristic scale μ (Eq. 27) is

$$\mu = \lambda\tilde{J} \quad [42]$$

Integrating $\tilde{j} = \kappa \exp(-z/\mu) = \exp(-z/(\lambda\tilde{J}))$ over $\tilde{z} \in [0, 1]$ and equating the result to \tilde{J} , after simple transformations we find

$$\tilde{J} = - \left[\lambda \ln\left(1 - \frac{1}{\lambda}\right) \right]^{-1} \quad [43]$$

In this regime the limiting current density of a cell is a function of λ only. Substituting this \tilde{J} into Eq. 42 we find

^aFrom Eq. 37 for large λ we get $\mu \sim \lambda$.

^bCalculation of the limit $\tilde{J} \rightarrow 0$ in the previous section is justified, because $\kappa = \kappa_0$ already at finite $\tilde{J} \approx \tilde{J}_0$ (Fig. 4b). For all curves in Fig. 4b the Tafel equation at $\tilde{J} = \tilde{J}_0$ is valid.

$$\mu = - \left[\ln \left(1 - \frac{1}{\lambda} \right) \right]^{-1} \quad [44]$$

This value coincides with that obtained for the case of zero crossover $\beta = 0$ (cf. Eq. 34). Using Eq. 44 in Eq. 26 and 28 we find

$$\tilde{\psi} = \tilde{\xi} = \tilde{j} = \left(1 - \frac{1}{\lambda} \right)^{\tilde{z}} \quad [45]$$

All variables in the cross—linked regime are universal functions of λ only.

Physically, the regime of cross-linked feeding is equivalent to the case of ideal membrane with zero crossover. Inlet concentrations and fluxes of reactants on both sides of the cell are matched so that methanol and oxygen concentrations in the respective catalyst layers tend to zero at any z .

Oxygen and Methanol Utilization, Mean Crossover Current

Mass balance equations (Eq. 7 and 8) lead to of integral relations, which are valid regardless of the distribution of local current density. These equations show that the rates of oxygen and methanol consumption differ only by a constant factor. Equating the left sides of Eq. 7 and 8 and integrating the result over $[0, \tilde{z}]$, we get

$$\lambda^a(\tilde{\psi} - 1) = \lambda^c(\tilde{\xi} - 1) \quad [46]$$

Introducing oxygen and methanol utilization according to $u^c(\tilde{z}) = 1 - \tilde{\xi}$, $u^a(\tilde{z}) = 1 - \tilde{\psi}$, respectively, we immediately find that

$$\frac{u^a(\tilde{z})}{u^c(\tilde{z})} = \frac{\lambda^c}{\lambda^a} \quad [47]$$

Though u^a and u^c depend on \tilde{z} , their ratio does not. In case of $\lambda^c = \lambda^a$ oxygen and methanol utilizations are equal: $u^c = u^a$. Putting $\tilde{z} = 1$ in Eq. 47 we get the ratio of total methanol and oxygen utilizations: $u^a(1)/u^c(1) = \lambda^c/\lambda^a$.

Integrating Eq. 8 over $\tilde{z} \in [0, 1]$ and taking into account that $\int_0^1 \tilde{j} d\tilde{z} = \tilde{J}$, after simple calculations we find

$$\frac{\tilde{J}_{\text{cross}}}{\tilde{J}} = \lambda^c u^c(1) - 1 = \lambda^a u^a(1) - 1 \quad [48]$$

where $\tilde{J}_{\text{cross}} = \int_0^1 \tilde{j}_{\text{cross}} d\tilde{z}$ and the last equality was obtained with Eq. 47.

The flux of methanol through the membrane is usually calculated measuring the amount of CO_2 in the cathodic exhaust.^{4,5} This method, however, is not reliable because CO_2 permeates through the membrane from the anode to the cathode side.⁴ Eq. 48 provides a simple means for evaluation of the overall crossover current in DMFCs: by measuring oxygen and/or methanol concentration at the outlet one can calculate \tilde{J}_{cross} with Eq. 48.

When crossover is zero, from Eq. 48 we find

$$u^c(1) = \frac{1}{\lambda^c}, \quad u^a(1) = \frac{1}{\lambda^a} \quad [49]$$

These relations do not depend on the type of feed molecules and are thus valid for hydrogen fuel cells.

Discussion

Formation of the bridge is essentially a 2D effect. As shown previously, a large value of voltage loss at open circuit cannot be explained within the scope of the 1D model. Furthermore, a 1D model cannot explain the dependence of E_0 on oxygen stoichiometry, detected in experiments of Qi and Kaufman.³ Our model explains the effect: the explicit dependence of E_0 on λ gives Eq. 38 with κ_0 , Eq. 36. The bridge manifests itself as a plateau on the cell polarization curve in the range of small currents (Fig. 2a). Physically, this plateau is due to the constant and independent of \tilde{J} local current density in the bridge. Detailed analysis shows that the length

of this plateau decreases with the growth of oxygen stoichiometry. Our recent experiments confirm the effect (to be published elsewhere).

In general, numerical models of DMFCs similar to those developed by Wang and Wang¹⁰ and Birgersson *et al.*¹⁶ should capture formation of the bridge. The characteristic size of the bridge μ is small and decreases with \tilde{J} , so that to resolve the bridge a fine grid in z direction is necessary.

Large E_0 does not necessarily mean poor cell performance in the whole range of currents. If conditions (Eq. 41) are satisfied, the cell with large E_0 exhibits excellent performance near the limiting current density.

The model above does not take into account formation of CO_2 bubbles on the anode side. At high current density these bubbles seriously affect transport of liquid methanol in the channel. Conditions Eq. 41 should, therefore, be considered as a qualitative hint how to minimize crossover.

The regime close to the cross-linked feeding was presumably realized in experiments.^{6,13} In Ref. 6 voltage loss due to crossover was less than 20 mV at 100 mA cm⁻². This small value indicates low methanol concentration in the anode catalyst layer.

Conclusions

A 1D + 1D model of a DMFC is developed. In case of equal oxygen and methanol stoichiometries the analytical solution to model equations is obtained. The solution exhibits a new effect: formation of a narrow bridge of a local current close to the inlet of the feed channels. The current density in the bridge remains finite even at vanishingly small current in the external circuit. The bridge thus “short circuits” DMFC electrodes.

Physically, formation of the bridge induces finite overpotentials on both sides of the cell and the cell OCV appears to be well below thermodynamic value. The voltage loss due to the bridge is given by Eq. 38.

The model suggests the regime of cell operation with zero methanol crossover. This regime is realized if at the inlet oxygen and methanol fluxes across the respective backing layer are equal and the cell operates close to the limiting current density. Under these conditions methanol concentration in the anode catalyst layer tends to zero and crossover is zero regardless of the transport properties of the membrane.

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List of Symbols

\sim	tilde marks dimensionless parameters; for their definition see Eq. 5
b	Tafel slope, V
c	total molar concentration in the channel, mol cm ⁻³
c_{ref}	reference molar concentration, mol cm ⁻³
D_b	Diffusion coefficient of feed molecules in the backing layer, cm ² s ⁻¹
E	total voltage loss, V
F	Faraday constant
i^*	exchange current density per unit volume, A cm ⁻³
J	mean current density in a cell, A cm ⁻²
J_{cross}	mean crossover current in a cell, A cm ⁻²
j	Local current density in a cell, A cm ⁻²
j^*	characteristic current density, A cm ⁻²
j_{lim}	limiting current density, A cm ⁻²
h	Channel height, cm
l_i	thickness of the catalyst layer, cm
l_b	thickness of the backing layer, cm
l_m	thickness of the membrane, cm
L	channel length, cm
N_{cross}	molar flux of methanol through the membrane, mol cm ⁻² s ⁻¹
p	ratio of Tafel slopes, $p = b^c/b^a$
q	dimensionless parameter (the definition is below Eq. 18)
R_n	contact resistance, Ω cm ²
u	feed molecules utilization
V_{cell}	cell voltage, V
V_{oc}	thermodynamic OCV, V
v	velocity of the flow in the channel, cm s ⁻¹

x coordinate across the cell, cm
 z coordinate along the channel, cm

Greek

α dimensionless parameter (the definition is below Eq. 18)
 β dimensionless parameter of crossover, Eq. 4
 β_1 $\beta_1 = \beta/(1 + \beta)$
 γ dimensionless parameter (the definition is below Eq. 18)
 η polarization voltage, V
 κ dimensionless local current density at the inlet
 λ stoichiometry of feed flow
 μ dimensionless characteristic scale of the exponent
 ξ oxygen molar fraction in the channel
 σ_1 proton conductivity of membrane phase in the catalyst, $\Omega^{-1} \text{ cm}^{-1}$
 ψ methanol molar fraction in the channel

Superscripts

0 inlet (at $z = 0$)
 a anode side
 c cathode side

Subscripts

0 at zero current
 b backing layer
 lim limiting

m membrane
 t catalyst layer

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