Diffusion Polarization in Air Channels

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Introduction

Rates of cathodic oxygen reduction, that is, cell currents are dependent on partial pressures of the oxidant if rate-controlling steps involve the concentration or partial pressure of oxygen. This is likely to be observed since reaction rates will be either liquid film or gas diffusion controlled. However, cases can arise where removal of the reaction product may be hindered by slow transport processes, thus resulting in, possibly, appreciable lower rates. This could be the case of water removal from the catalyst surface of an oxygen electrode. If local current densities are either dependent on partial pressures of oxygen or water, it will become necessary to establish relationship predicting such local current densities and to design electrode geometries favorable to uniform current distribution, and as a result uniform distribution of the main influential variables affecting oxygen electrode performance. Such considerations, however, would imply knowledge of limiting current densities.

In restablishing over-all oxygen electrode capabilities for fuel cell application, one of the important variables is the limiting current density. Although these limiting currents are not simply dependent on some limited parameters, i.e. electrode activity, electrode structure, electrolyte properties, local temperatures, anisotropic current density distributions, etc..., actual measurements are valuable if some reproducible characteristics can be controlled, i.e. catalytic activity, electrode structure, electrolyte properties. Thus, measurements are valuable for a specifically designed system, as related to limiting current densities, and very generally applicable to any air electrode current collector design, if the geometry is influential on, and descriptive of, the limiting currents.

The ultimate goal, that is quantitative description of current-voltage relationships as a function of main variables, can be, in principle, attained from experimental studies, involving the determination of limiting current densities at discrete positions in the channels, the establishment of the rate-controlling process for known channel geometries in the high current density range (corresponding to 0.85 - 0.5 volts), the derivation of relationships describing the current-voltage behavior over practical operational ranges, the transport phenomena explaining polarization potentials at these practical currents and the experimental values of open circuit potentials. If all these equilibrium conditions, rates and processes are known, a reasonable analytical description of local as well as over-all currents and potentials, can be expected.

It is possible then, that limiting currents can be associated with channel geometry and that diffusional processes in restricted channels become small enough i.e., rate-controlling.

The purpose of the present work was to obtain experimental results and interpretation to explain polarization in channels of defined geometry and to establish influential parameters which would affect electrode performance. In order to establish applicability of a self-breathing air electrode, viz. without forced convective air-flow, for low current densities, experimental investigations were started on straight air channels. Furthermore, since such a self-breathing electrode had to operate away from limiting currents, in order to minimize diffusion polarization, additional work for forced flow (at various air flow rates) was conducted in straight air channels. This work will be reported elsewhere. (2)

Experimental Equipment

The system chosen for experimental investigation was based on platinum black electrodes associated with a solid-matrix electrolyte (cation exchange membranes). Such a system offered multiple advantages in preparing discretely separated small electrodes, displaying good and uniform contact with the electrolyte. The individual electrodes included metallic screens in order to increase surface conductivity.

Reference potential measurements were based on a Luggin-type capillary-SCE system, specially developed for application to ion exchange membrane electrolytes (1). A low-leakage capillary was placed against the membrane and sulfuric acid used to establish the bridge with the calomel electrode. In all cases, the ion exchange membrane extended outside of the apparatus for potential measurements. Effects of capillary positions were investigated by placing the tip against and within the membrane. No appreciable differences were observed.

The ten segmented electrodes allowed the determination of limiting currents as a function of position and represented values for discrete electrode sizes. In many instances, the presented data will represent smooth interpolation of position-dependent limiting currents.

Investigations were conducted under galvanostatic operating conditions. The equipment is represented in Figure 1. All experimental work was conducted on air channels 2-1/2" long and 1/2" wide. Channel height could be varied by changing a removable Lucite bar placed on the channel top. Thus, channel heights could be 1/16, 1/8, 1/4 and 1/2". The channel was mounted on an air electrode and placed in a large Lucite box in order to avoid small air flow sweeps over the air electrode. Both channel ends were open to allow for oxygen diffusion.

In order to determine local current densities, the air electrode was manufactured by placing ten parallel electrode/screen strips on an Ion Exchange Membrane. Gaps of 1/16" between electrodes allowed for electrical insulation of the various electrodes. Electrode dimensions were 1/2" x 3/16" with an actual area of $0.60 \pm 0.05\ cm^2$. The Ion Exchange Membrane extended out of the channel for reference potential measurements and stainless rods contacted the screens for current pick-up.

The counter electrode (H_2-electrode) was prepared in a similar manner. Catalytic electrodes faced each other across the electrolyte (membrane).

The two ends of the self-breathing channel were open, thus displaying planar symetry on either side of the channel center cross-section. Closing one channel end actually corresponded to doubling the channel length. Single electrode failure would not affect results too appreciably since experimental results could be obtained from mirror-image electrode.

Experimental Results

Representative single electrode polarization characteristics are presented in figure 2 for a channel height of 1/16". These polarization curves represent the largest changes from the edge to center electrodes for the smallest channel height investigated.

EXPERIMENTAL DEVICE FOR MEASUREMENTS OF LOCAL CURRENTS IN AIR CHANNELS OF VARIABLE GEOMETRY

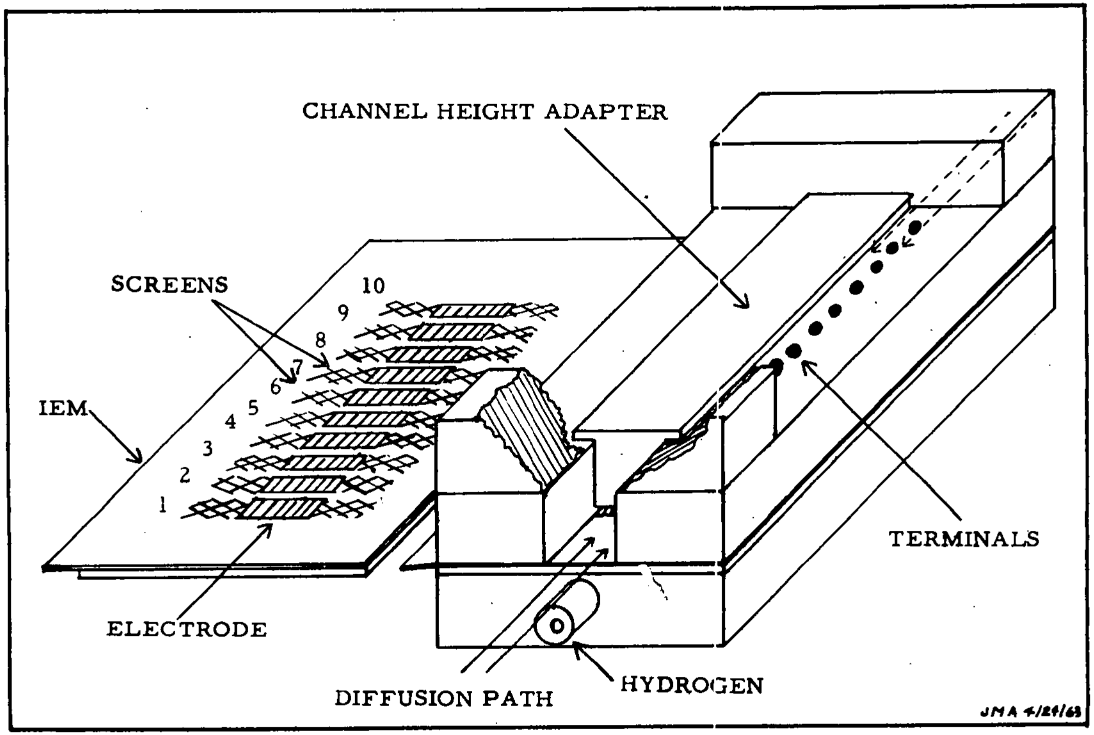


FIGURE 1

POLARIZATION CHARACTERISTICS OF INDIVIDUAL ELECTRODES FOR TEN PARALLEL ELECTRODES - CHANNEL HEIGHT: 1/8" ELECTRODE SURFACE: $0.6 cm^2$

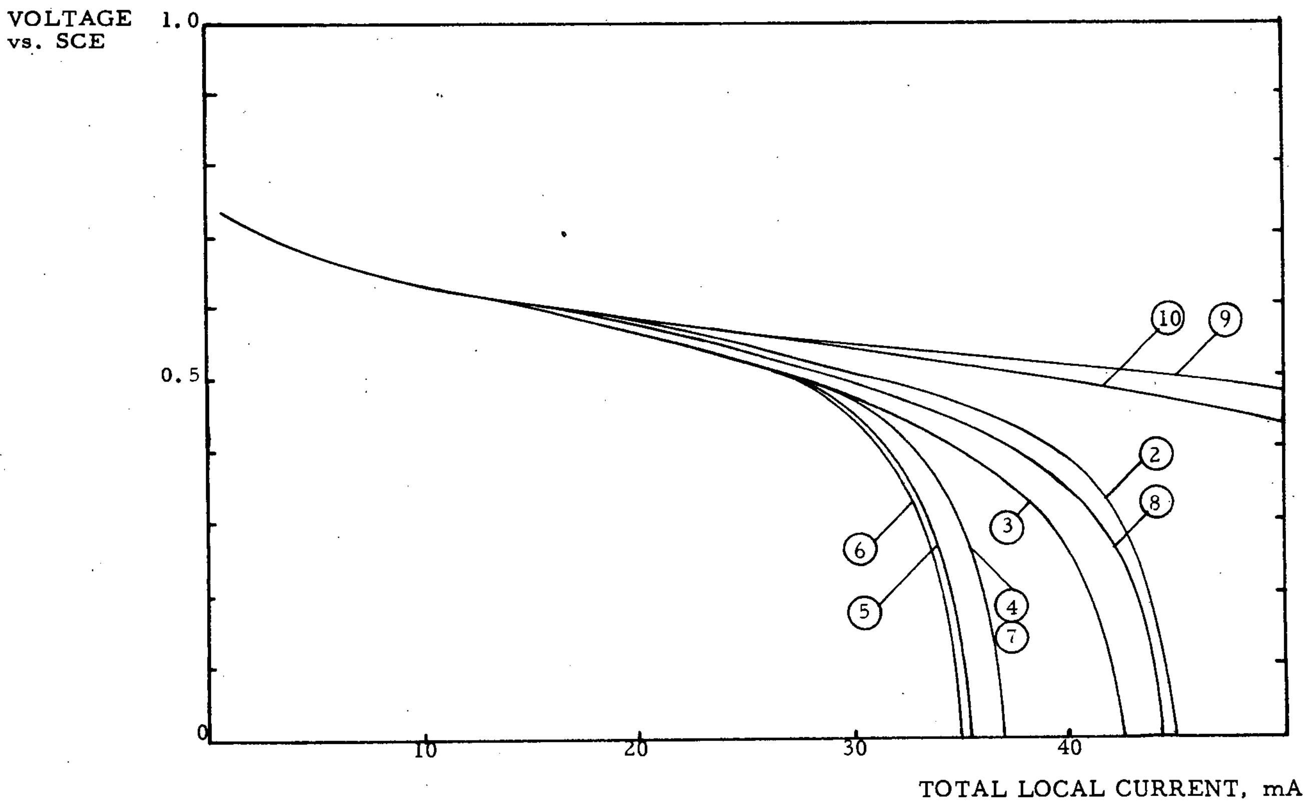


FIGURE 2

CURRENT DISTRIBUTION FOR INDIVIDUAL ELECTRODES IN THE SELF-BREATHING CHANNEL - ELECTRODE SURFACE: 0.6 cm^2. CHANNEL HEIGHT: 1/8"

LOCAL CURRENT mA

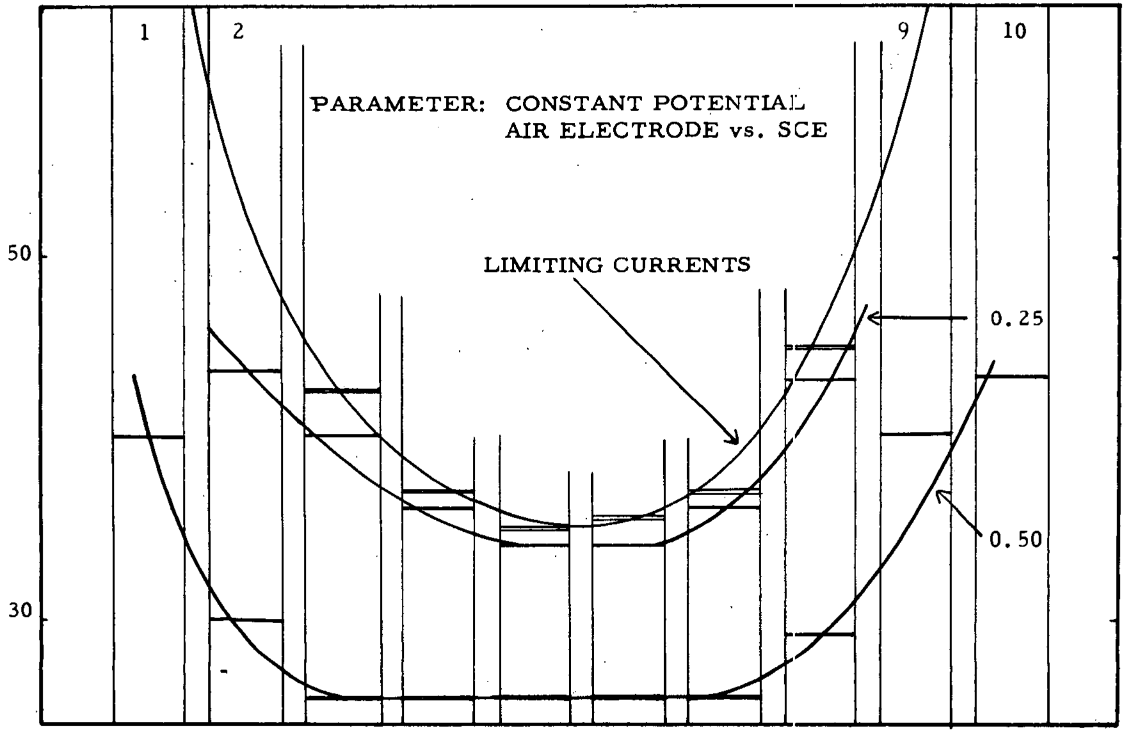


FIGURE 3

CURRENT DISTRIBUTION FOR INDIVIDUAL ELECTRODES IN THE SELF BREATHING/CHANNEL-ELECTRODE SURFACE: 0.6 cm^2. CHANNEL HEIGHT: 1/16"

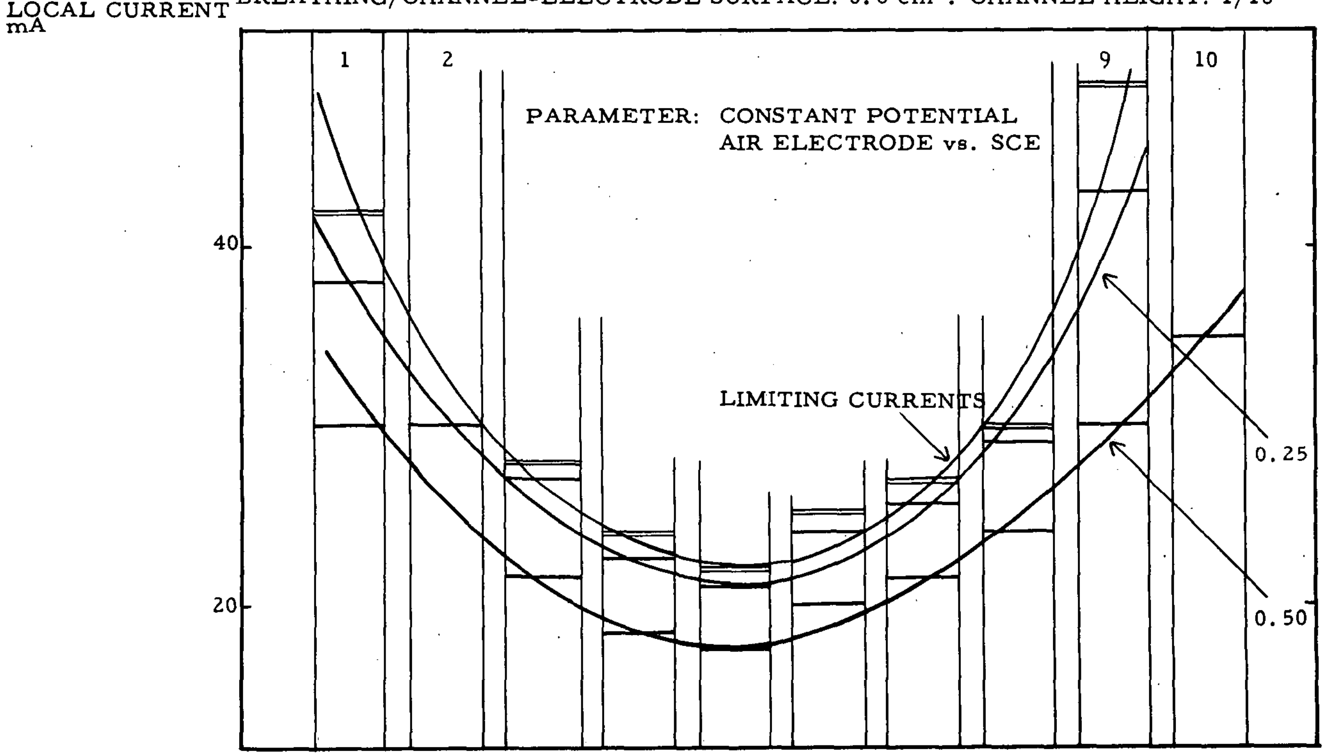


FIGURE 4

Limiting current densities for edge electrodes # 1 and 10 should be about 130-140 ma/cm^2 (as determined independently for electrodes exposed to semi-infinite air space).(2) Figure 2 already indicates that appreciable polarization is encountered as soon as measurements are conducted slightly away from the channel edge. Larger currents are observable for all electrodes for increasing channel height. For 1/2" channels, very little polarization is observable even at current densities near limiting values, i.e. 130-140 ma/cm^2. Polarization is less severe for all electrodes at small local currents, as expected.

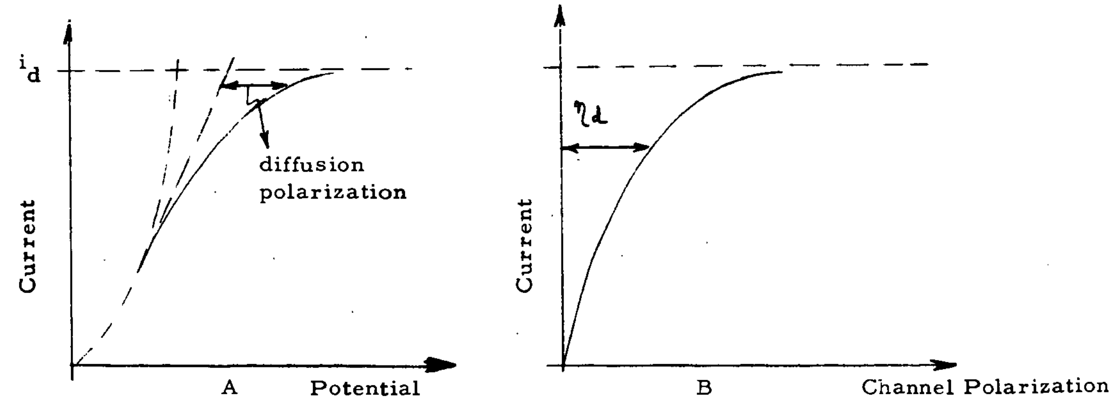
Channel heights affect polarization characteristics to a large degree, i.e. limiting currents for center electrodes are 22 and 35 ma, for 1/16" and 1/8" channels, respectively. These current densities correspond to oxygen partial pressures of 0.07 to 0.1 respectively, as determined independently from exposed electrode measurements.

For identical polarization potentials (as determined for polarization curves) current density distributions display minima for inner electrodes and can be extrapolated to edge values of limiting currents as determined from previous measurements. Strictly speaking these current densities can not be described from figure.2.However, the partial pressure of oxygen in the channel would not be too greatly affected at higher current corresponding to limit currents of the edge electrodes. Results would be affected greatly at the edge electrodes, let's say electrodes 1 and 2 and their corresponding symetrical position.

Current density distributions for channel heights of 1/8 and 1/16" for various applied potentials are represented in figures 3 and 4. Edge currents (about 80 mA) can become 2 to 4 times larger than center channel currents, but display much more uniform distribution for lower electrode polarization, i.e. 0.5 volt vs. SCE for 1/8" channel.

Interpretation of Individual Polarization Curves

Current potential behavior for the investigated systems can be represented by Figure 5.



i_d = diffusion-limited current

channel polarization η_d = Ea - E wce = Actual Voltage-voltage in absence of channel effects.

SINGLE ELECTRODE DIFFUSION POLARIZATION

Figure 5

Figure 5A represents polarization characteristics as observed in absence and presence of diffusion polarization (including activation polarization, in absence of ohmic contribution, which are generally eliminated). Figure 5B represents strictly diffusion polarization terms in absence of other possible polarization.

Polarization characteristics can be represented by the equation:

$$\left(1 - \frac{i}{i_L}\right) = e^{\alpha(E^\circ - E)} \qquad (1)$$

where i and i_L represent actual and limiting currents, respectively; $\alpha = \beta \mathcal{F}/RT$, E^o = reference potential in absence of channel polarization, $E^o - E = \eta_d$

$$\mathrm{Ln}\left(1 - i/i_L\right) = \alpha(E^\circ - E) = \alpha \eta_d \qquad (2)$$

By differentiation:

$$\frac{dE}{di} = \frac{1}{\alpha i_L (1 - i/i_L)} \qquad (3)$$

with

$$\left(\frac{dE}{di}\right) \rightarrow \infty \text{ as } i \rightarrow i_L$$

and

$$R_d = \left(\frac{dE}{di}\right)_{i=0} = \frac{1}{\alpha i_L} \qquad (4)$$

Since $i_L(x)$ displays a monotonous decrease up to channel center, equation 4 is expected to display an increase from channel edge to center. Figure 6 represents smoothed experimental results for 1/4, 1/8 and 1/16" channel heights. Since no additional position-dependent polarization was observed for 1/4" channels, the value $R_d = 4$ was chosen as reference systems resistance to obtain a relationship between channel-induced diffusion resistance $R_d(x)$ and $i_L(x)$. Now, in equation (4), the slope (dE/di) defined as diffusional resistance becomes dependent on α and i_L. (If i_L can be determined analytically and since α represents defined constants, $(dE/di)_L$ is defined). Equation 4, if represented by $\left(\frac{1}{i_L}\right)/\left(\frac{\Delta V}{\Delta i}\right)$ should yield a constant value, determining α. $\left(\frac{\Delta V}{\Delta i}\right)$ representing the diffusional resistance should display:

a. no diffusional resistance at the edges, at least as related to electrode geometry
b. maximum diffusional resistance for center electrodes
c. increased resistance for reduced channel cross-section

Experimental results regarding these observations are represented in Table I for channel heights of 1/8 and 1/16", and different electrode positions.

SLOPES ($\Delta V/\Delta I$) FOR VARIOUS ELECTRODES IN THE SELF-BREATHING AIR ELECTRODE CHANNEL

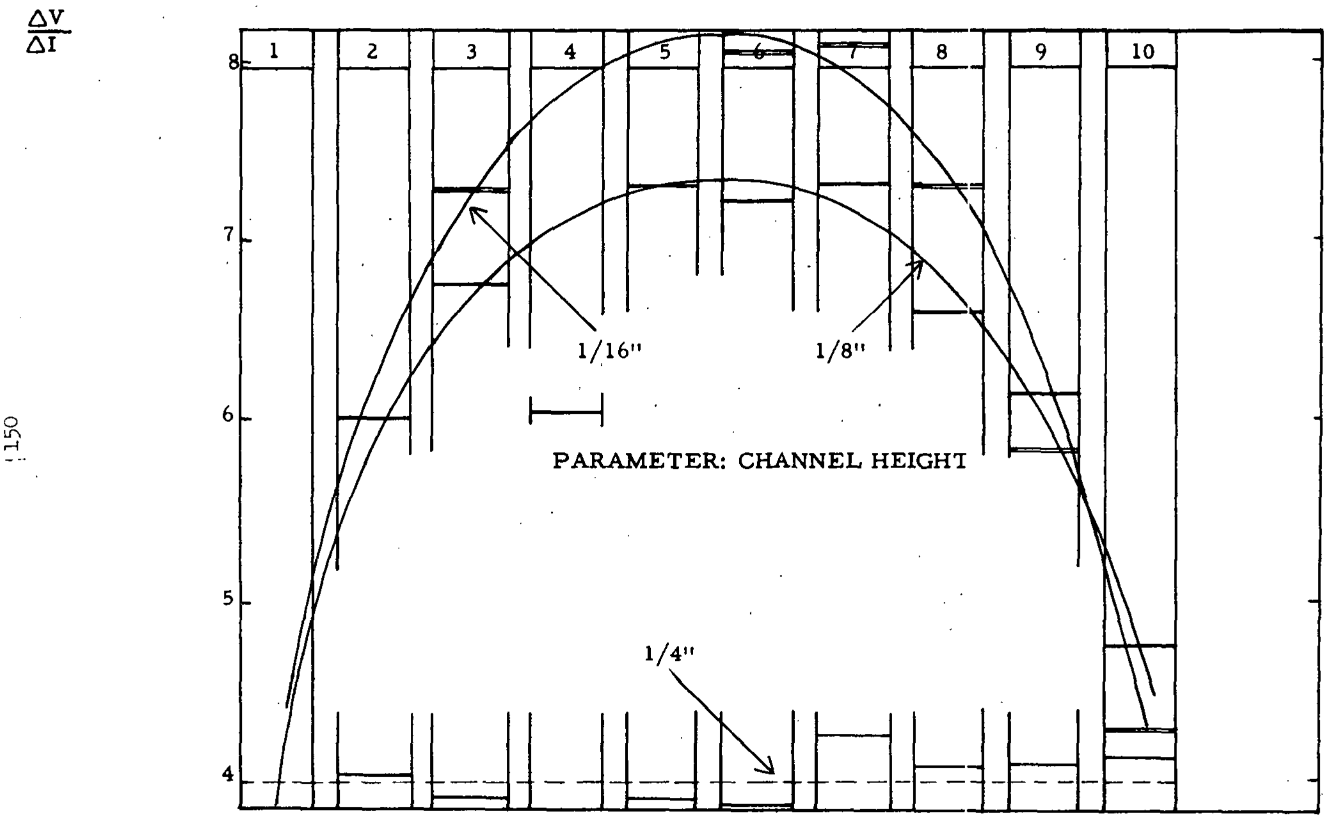


FIGURE 6

TABLE I

Determination of α from experimental data

Electrode Position	Limiting Current, i_L Amps.	$1/i_L$ $(\text{Amps})^{-1}$	$\left(\frac{\Delta V}{\Delta I}\right)_{exp.}$ (ohm)	$\left(\frac{\Delta V}{\Delta I} - R\right)$ (ohm)	$\frac{1}{(\Delta V/\Delta I - R)}$ $(\text{ohm})^{-1}$
Channel Height 1/16"					
1	0.041	-	-	-	-
2	-	-	-	-	-
3	0.028	35.8	7.3	3.3	10.8
4	0.024	41.7	7.8	3.8	11.0
5	0.022	45.5	8.2	4.2	10.8
6	0.025	40.0	8.1	4.1	9.8
7	0.027	38.0	7.9	3.9	9.7
8	0.030	33.3	7.3	3.3	10.1
9	~ 0.050	~ 20.0	6.1	2.1	9.6
				Average α	= 10.4
Channel Height 1/8"					
1	-	-	-	-	-
2	0.045	22.2	6.0	2.0	11.1
3	0.043	23.2	6.7	2.7	8.6
4	0.037	27.0	7.1	3.1	9.0
5	0.035	28.6	7.3	3.3	8.7
6	0.035	28.6	7.3	3.3	8.7
7	0.037	27.0	7.1	3.1	9.0
8	0.044	22.7	6.8	2.8	8.2
				Average α	= 9.0

Since the coefficient α represents actually $\beta\mathcal{F}/RT$ in equation 1, average values of β as determined from Table I would be 0.24-0.27.

Now, since α has been obtained experimentally and represents values near theoretical, a complete description of the polarization curves will be available, providing $i_L(x)$ can be established.

Evaluation of the limiting current $i_L(x)$

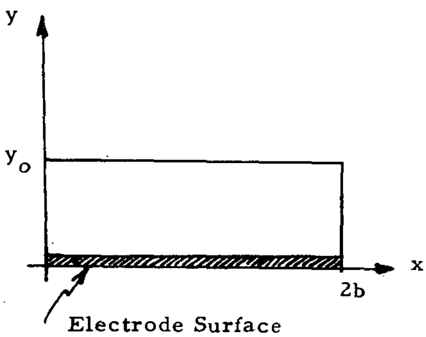
The analytical evaluation of $i_L(x)$ will allow the description of the polarization curves by means of equation 4. Local limiting currents can be evaluated by solving Laplace's equation, providing transport by convection is considered to be negligible.

A. Determination of concentration distribution in channels

$$\nabla^2 C_i = 0 \qquad (5)$$

$$\sum_i C_i = 1 \qquad (6)$$

C_i represents partial pressures in the three component systems. Boundary conditions are:



$$\left.\begin{aligned} C_i(0,y) &= C^i \\ C_i(2b,y) &= C^i \end{aligned}\right\} \text{B.C. 1}$$

$$\left.\begin{aligned} C_{O_2}(x,0) &= 0 \\ C_{N_2}(x,0) &= 1-f(T) \\ C_W(x,0) &= f(T) \end{aligned}\right\} \text{B.C. 2}$$

$$\frac{dC_{O_2}}{dy} = \left.\frac{dC_{N_2}}{dy}\right|_{y=y_0} = 0 \qquad \text{B.C. 3}$$

$$\left.C_{O_2} + C_{N_2}\right|_{y=y_0} = 1 - g(T) \qquad \text{B.C. 4}$$

The concentration of component (i) is related to the partial pressure by:

$$C_i = \frac{n_i}{V} = \frac{p_i}{RT} \qquad (7)$$

Solutions of equation 5 are, for the different components:

$$C_{O_2} = C^0\left[1 - \sum_{n=1} A_n \sin\alpha_n x\left(\cosh\alpha_n y - \operatorname{th}\alpha_n y_0 \operatorname{sh}\alpha_n y\right)\right] \qquad (8)$$

$$C_W = \sum_{n=1} A_n \sin\alpha_n x\left[\frac{g(T) - f(T)\cosh\alpha_n y_0}{\operatorname{sh}\alpha_n y_0}\operatorname{sh}\alpha_n y + f(T)\cosh\alpha_n y\right] \qquad (9)$$

with $A_n = \frac{(-1)^n - 1}{b\alpha_n}$ and $\alpha_n = \frac{n\pi}{2b}$

where g(T) and f(T) represent partial pressures of water under equilibrium conditions at $y = y_o$ and $y = 0$, respectively.

Local current densities can now be obtained from:

$$j(x) = -n\mathcal{F}\mathcal{D} \left. \frac{dC_{O_2}}{dy} \right|_{y=0} \qquad (10)$$

and are, (for O_2 diffusion):

$$j(x)_{O_2} = -n'\mathcal{F}\mathcal{D}c^o \sum_{n=1} \alpha_n A_n \sin \alpha_n x \, \mathrm{th}\, \alpha_n y_o \qquad (11)$$

and for H_2O diffusion:

$$j(x)_w = -n'\mathcal{F}\mathcal{D} \sum_{n=1} \alpha_n A_n \sin \alpha_n x \left[\frac{g(T) - f(T) \cosh \alpha_n y_o}{\mathrm{sh}\, \alpha_n y_o} \right] \qquad (12)$$

Average channel current densities are:

$$J_{Ave.\,O_2} = \frac{n'\mathcal{F}\mathcal{D}c^o}{b\pi} \sum_{n=1} \frac{[(-1)^n - 1]^2}{n} \mathrm{th}\left(n\pi \frac{y_o}{2b}\right) \qquad (13)$$

and

$$J_{Ave.\,H_2O} = \frac{n'\mathcal{F}\mathcal{D}}{b\pi} \sum_{n=1} \frac{[(-1)^n - 1]^2}{n} \left[\frac{g(T) - f(T) \cosh \alpha_n y_o}{\mathrm{sh}\, \alpha_n y_o} \right] \qquad (14)$$

B. Application to specific environmental conditions

For operation with air, equations 11 and 12 become:

$$j(x)_{O_2} = 0.235 \sum_{n=1,3..} \sin\left(n\pi \frac{x}{2b}\right) \mathrm{th}\left(n\pi \frac{y_o}{2b}\right) \qquad (15)$$

$$j(x)_w = 0.031 \sum_{n=1,3..} \sin\left(n\pi \frac{x}{2b}\right) \left[\frac{1 - \cosh \alpha_n y_o}{\mathrm{sh}\, \alpha_n y_o} \right] \qquad (16)$$

Equation 15 and 16 are based on:

$\mathcal{D}_{O_2} = 0.21 \ cm^2/sec$

$\mathcal{D}_w = 0.29 \ cm^2/sec$

g(T) = h(T) = 30mmHg (vapor pressure of water at 30°C)

n' = number of equivalent/mole
$\mathfrak{F}$ = Faraday constant = 96, 500
2b = channel length = 6.35 cm
y_o = channel height = 0.32 and 0.16 cm

Some calculated data are presented in Table II for a channel height of 1/16".

Table II

Local Current Density for 1/16" channel height

	Position	Local current density j(x) in mA/cm^2	j(x)/j(x) min.	Minimum Current density j(x) min.
Oxygen Diffusion	b	117	1.0	
	b/2	163	1.41	117
	b/4	298	2.55	
Water Diffusion	b	20	1.0	
	b/2	22	1.1	20
	b/4	35	1.7	
Measured	b	38	1.0	
	b/2	44	1.2	38
	b/4	61	1.6	
	0	110	2.9	

Calculated and experimental results are presented in figure 7 for the 1/16" channel and for fixed diffusion coefficients. Data can be represented fairly well by assuming a water diffusion-controlled process.

Discussion

Restriction of channel cross-section, i.e. of y_o, may result in appreciable reduction in gas-phase transport rates. In fact these rates may be calculated from purely gas-diffusion controlled processes. In channel where forced air-flow rates may be small, unfavorable current density distribution may also be encountered. The results also suggest reduction of channel length (for defined y_o) in an attempt to maintain quasi-uniform oxygen partial pressure and surface temperature. The results indicate applicability of self-breathing electrodes up to about 25 mA/cm^2 (at ambient temp.) in a design where air-electrodes would be disposed face-to-face and separated by air-channels such that $y_o \gg 1/4"$. Better current distribution may also be expected for disc-shaped electrodes, by careful selection of the channel-gap/electrode-radius ratio.

CURRENT DISTRIBUTION IN 1/16" CHANNEL

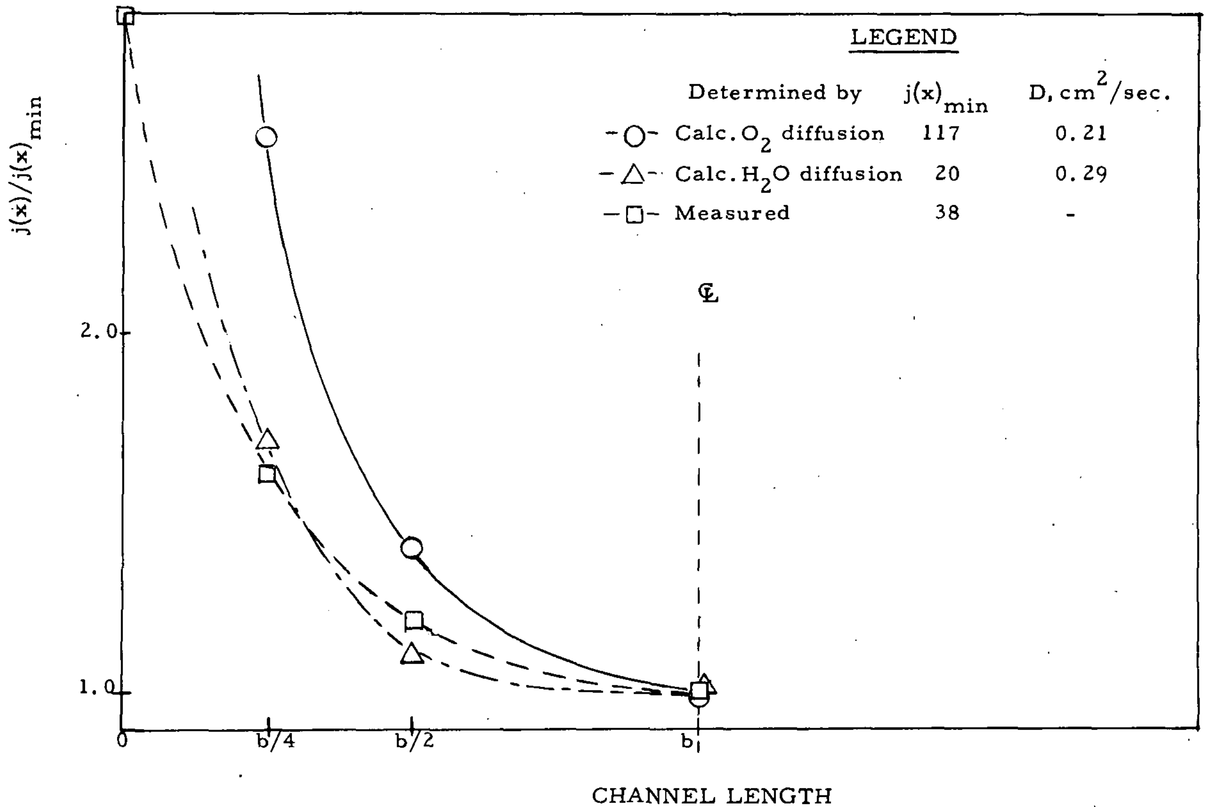


FIGURE 7

Application

This section will include application of previous results to a system where channel length has been reduced, that is results on perforated sheets as cathodic current collector. (3)

One figure will be added as reported at the Power Sources Conference. (4)

References:

1. "Ion Exchange Membrane Fuel Cell - #3". U.S. Army Signal Corps Res. and Dev. Lab., Ft. Monmouth, N. J. Sept. 1962. ARPA No. 80.

2. Ibid. - Report #2, June 1963. "Current Distribution in Air-Breathing Electrode Channels Under Forced Flow Conditions."

3. Ibid. - Report #2, June 1963 - J. Dankese: "Heat and Mass Transfer Investigations of the Air-Breathing IEM Fuel Cell."

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