DOE/RL/00600--T1

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Date

MECHANISMS AFFECTING MASS TRANSFER IN FUEL CELLS

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March 15, 1982

DOE/RL/00600--T1

DE82 013431

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82-9E3-EGGCP-P1
Unrestricted

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MECHANISMS AFFECTING MASS
TRANSFER IN FUEL CELLS

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ABSTRACT

An initial analysis of particulate effects on molten carbonate fuel cells has been conducted. The analysis has been applied to a conceptual fuel cell with operating parameters appropriate to use with future power generation plants. Particle transport due to several mechanisms has been considered and dominant mechanisms affecting particle delivery to anode channel surfaces and into anode pores have been identified. Thermophoresis and gas flow out from anode pores have been found to inhibit particle arrival on the anode and entry into pores so that neither anode channel blockage nor pore blockage are expected for particles with diameters smaller than about one micron. The analytical approach developed could be applied to other fuel cell types in addition to the molten carbonate fuel cells.

INTRODUCTION

Fuel cells are being considered for future power generation. Because the electrochemical processes by which fuel cells generate power do not involve fuel combustion and associated Carnot cycle efficiency limitations, future power plants operating with fuel cells may be substantially more efficient than current fossil fuel power plants. One source of fuel for future fuel cell power plants is gasified coal. Although the coal gas will be cleaned with highly efficient scrubbers or filters, limited quantities of particulates will be entrained in the gases entering the fuel cells. Possible blockage of fuel cell anode pores by particles has been perceived to be a significant potential problem and it has been suggested⁽¹⁾ that a safe particle concentration for fuel cell applications should be "essentially zero." However, since there appears to be no theoretical or experimental results reported in the open literature concerning particulate effects on fuel cells, their tolerances to particles are unknown and there is little basis for specifying acceptable particle concentrations.

The intent of this study is to provide an initial theoretical treatment of fuel cell deposition and a foundation for more detailed theoretical efforts in the future. Dominant mechanisms and factors controlling molten carbonate fuel cell deposition are identified. Existing electrochemical theoretical models for determining limiting currents generated in individual anode pores are extended to provide relationships for flow rates from anode pores which are determined to have a major effect on particle transport to anode surfaces and entry into pores. Areas are suggested for future theoretical efforts related to fuel cell deposition.

THE MOLTEN CARBONATE FUEL CELL

A molten-carbonate fuel cell bank consists of stacks of individual cells electrically interconnected to produce the desired power output at the required voltage. A section of a single molten carbonate cell is illustrated in Figure 1. The cell consists of two porous electrodes separated by a porous tile containing a liquid electrolyte made up of a mixture of alkali carbonates, all of which are sandwiched between separator plates. The separator plates function as current collectors and provide channels for fuel gas flow over the anode and oxidant gas flow over the cathode.

Fuel gas flows through the anode flow channels, penetrates into the anode pores, and fuel reactants H_2 and CO in the gas react with carbonate ions in the electrolyte which occupies the pores to produce electrons according to the following reactions:

The oxidation of CO by Eq. (2) is in competition with the more favored water-gas shift reaction which converts CO to H_2 :

The $CO_3^{=}$ ions utilized in the above reactions have migrated to the anode through the electrolyte after being produced in the cathode. The electrons generated in the anode travel by way of an external circuit to the fuel cell cathode to participate in the cathode reactions which produce the carbonate ions. The continuous generation and utilization of electrons according to the above reactions and their flow from the anode to cathode through an external circuit results in the fuel cell current output.

The conceptual molten carbonate fuel cell evaluated in this study has operating characteristics which are objectives of current development work⁽²⁾ for future power plants. The cell area is about $15,000\text{ cm}^2$ (16 ft^2) and produces an average power density of 0.135 watts/cm^2 (125 watts/ft^2) of cell area at an 0.8 V/cell potential. For operation with future power plants, the anode inlet gas pressure, temperature and percent H_2 and CO fuel utilization in anode channels are assumed to be 10 atmospheres, 650°C (1202°F), and 85%, respectively.

FIG. 1 - Molten carbonate fuel cell section

FUEL CELL ANODE MODEL

The theoretical models here utilized to represent fuel cell anodes are similar to models which have been successfully used for fuel cell electrochemical analyses.^(3,4) Figure 2 represents the molten carbonate fuel cell anode. Fuel gas flows parallel to the anode surface. Reactant species H_2 and CO from the gas enter the anode pores and diffuse through the electrolyte in the pores to the pore walls where reactions given by Eq. (1) and (2) occur. Reaction products H_2O and CO_2 diffuse back through the electrolyte and out of the pores into the fuel gas flow.

The distribution of electrolyte in the anode pores is considered to be governed only by capillary absorption which progresses from smaller to larger pore sizes.⁽⁵⁾ All pores smaller than an equilibrium pore diameter (associated with a balance of capillary and pressure forces) are assumed to be flooded and all pores larger than the equilibrium diameter are assumed to be virtually empty except for a thin film of electrolyte on the pore walls. Different pore models and resulting mathematical formulations describe the diffusion of reactant gas species for the flooded pores and thin film pores.⁽⁴⁾ Although an initial analysis⁽⁴⁾ suggested that thin film pores produce a substantial fraction of the electrons generated in molten carbonate fuel cell anodes, later experimental work has shown that most of the current is generated in the anode flooded pores.⁽³⁾ Fuel cell electrode performance measurements and post-test mercury porosimetry data associated with this recent work have provided evidence for the validity of the above described electrolyte distribution and electrochemical performance models.

MECHANISMS OF DEPOSITION

Particles entrained in the anode fuel gas can potentially degrade fuel cell performance by i) depositing on the anode flow channel surfaces to restrict anode channel gas flow, or ii) entering into and blocking anode pores to inhibit H_2 and CO reactant migration into the pores and H_2O and CO_2 reaction product migration out of the pores, driving reactions of Eq. (1) and (2) to the left (opposite to the desired direction). Pore blockage is of particular concern because anode pore diameters (a typical

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FIG. 2 - Anode pore representation

R.A. Wenglarz
d.m.s. - jd 12-22-81

Dwg. 7754A 84

average anode pore diameter is 5 microns) might be expected to be prone to blockage by particles of diameters from 0.1 micron up to 1-3 microns for which gas cleanup devices such as scrubbers and filters are least effective.

Mechanisms of particle transport in fuel cells are:

- Brownian diffusion
- Electrostatic migration
- Gravitational settling
- Thermophoresis
- Convection

Due to the small dimensions (typical height = 0.25 cm (0.1 in)) and low flow velocities (typical velocity less than 30 cm/sec (1 ft/sec)) for anode flow channels, flow is laminar and turbulent diffusion particle transport is not in effect. Particle deposition velocities have been determined for each of the above listed mechanisms acting alone to identify which dominate particle transport to anode flow channel surfaces and entrances to anode pores.

For Brownian diffusion, particle deposition velocities have been obtained at a location near the anode channel inlet (where particle arrival rates are higher than downstream) just beyond the region where the laminar flow velocity profile becomes approximately fully developed. Electrostatic migration velocities associated with diffusion charging of particles were determined since, for the 0.1 to 3 micron particle diameter range of concern, diffusion charge levels are much higher than for bombardment (field) charging in the low intensity (typically a few volts/cm) anode-cathode electrostatic force field. To determine thermophoretic deposition velocities, a thermal gradient associated with a 2°C (3.6°F) difference between bulk gas stream temperature and anode surface temperature was used based on results from thermal flux modeling of fuel cell channels. While Brownian diffusion, electrostatic migration, and gravitational settling tend to deliver particles to the anode surface, thermophoresis tends to transport particles away from that surface due to the direction of the thermal gradient. Because anode reactions of

Eq. (1) and (2) release heat at the walls of anode pores which is primarily absorbed by the metal anode, the anode temperature is higher than the flow channel gas temperature.

Convection effects also tend to transport particles away from the anode surface and affect particle entry into anode pores. As indicated earlier, the reactions of Eq. (1) and (2) are accomplished by migration of H_2 and CO from the anode flow channels into the pores, reaction of these species with $CO_3^{=}$ ions from the electrolyte, and diffusion of reaction products H_2O and CO_2 out of the anode through the pores into the anode fuel channels. The lower molecular weights of H_2 and CO entering the pores compared to H_2O and CO_2 exiting the pores results in a net mass flow out of anode pores which tends to inhibit particles delivered to the anode surface by other mechanisms from entering into the pores. Whether or not particles can enter into the pores and, if so, the rates of entry depend on the relative magnitude of forces delivering particles to the pores compared to the forces on particles due to the flow out of the pores.

Theoretical relations for flow rates out of pores will be later derived in following discussion of pore blockage by particles. However, it is here noted that the net flow rate from pores continually decreases in progressing from the anode channel inlet to exit. As fuel species H_2 and CO are utilized along the channel length, their decreasing concentrations result in lower production and flows of reaction products H_2O and CO_2 from pores.

The flow from pores not only inhibits particle entry into pores but also inhibits arrival on the anode surface. As particles near the anode surface are carried by the anode channel flow and slowly descend toward that surface due to the various particle transport mechanisms described above, these particles periodically pass through "jets" issuing from the pores. Each "jet" tends to slow, or even reverse, particle descent until it is traversed. Although the theoretical modeling and analysis of this complex flow and particle transport situation is beyond the intent of this initial assessment of fuel cell deposition, the net effect on particle delivery is here approximately

represented by using the total local mass flow per unit anode area to obtain an average local flow velocity from the anode which is assumed normal to the anode surface. By regarding the deposition velocity to be relative to the fluid flow, based on first order effects, arrival on the anode surface can be considered to be substantially inhibited, if not eliminated, if the local average pore velocity component from the anode surface exceeds the particle deposition velocity component toward the anode surface.

TRANSPORT TO ANODE SURFACES

Deposition associated with the transport of particles to the anode surface will be first discussed followed by consideration of particle transport into pores affected by flow convection from pores.

Figure 3 gives deposition velocities (mass arrival rates divided by gas stream particle concentrations) versus particle diameter for the various transport mechanisms affecting particle delivery to anode surfaces. The range of particle sizes given represents expected limits entering fuel cells from coal conversion processes after particulate removal with scrubbers or filter cleanup devices.

Also designated on the Figure 3 are average anode flow velocities (obtained in the next section) at locations at the anode channel inlet and at the channel exit. At the channel inlet, the average anode flow velocity exceeds deposition velocities for all mechanisms of transport to the anode surface so that particle delivery to the anode surface is substantially reduced, if not eliminated. At the channel exit, the average anode flow velocity is of the same order of magnitude as particle deposition velocities for particle diameters below one micron and is consequently expected to substantially reduce, if not prevent, particle arrival to the anode surface for this size range.

For regions near the channel exit and particles above about one micron in diameter, gravitational settling dominates the other mechanism of particle transport and the net movement for particles above this size is to the anode surface. However, for particle diameters below about one micron, thermophoretic transport of particles away from the anode surface

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Fig. 3 - Deposition velocities for molten carbonate fuel cells

R. Wenglarz
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is shown to be of the same order of magnitude as the other mechanisms which transport particles to the anode surface. Consequently, thermophoresis, in addition to the average flow from pores, can prevent, or at least greatly decrease deposition on flow channel anode surfaces for particle diameters smaller than about one micron.

TRANSPORT INTO PORES

Figure 4 represents a particle which has been delivered to the vicinity of a pore entrance by one of the mechanisms described above with a deposition velocity V_d relative to the local gas. The local flow velocity of gas exiting the pore due to reactions of Eq. (1) and (2) at the pore walls is designated U_p . If the local flow velocity U_p exceeds the the particle deposition velocity V_d relative to the flow, then the particle does not enter into the pore. If V_d is greater than U_p , then the net particle movement is into the pore where it can deposit. For the purposes of this initial analysis, detailed characteristic of pore flow such as pore velocity profile will not be considered; particle penetration into the pore will be attributed to the particle deposition velocity exceeding the average flow velocity from the pore for diameters of pores significantly larger than particle diameters. Relations for average pore flow velocity versus pore diameter are derived in the following section.

Pore Flow Velocities

The mass flow rate Q from a pore with cross sectional area A_p is related to average pore velocity U_p and gas density ρ_g by

$$Q = \rho_g U_p A_p$$

Solving for U_p ,

$$U_p = Q / \rho_g A_p \quad (3)$$

For $\dot{N}_\alpha$ designating the net mole flow rate of species α out of the pore and μ_α designating the mass per mole of species α ,

$$Q = \sum_{\alpha} \dot{N}_\alpha \mu_\alpha \quad (4)$$

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FIG. 4 - Particle transport near pores

R.A. Wenglarz
m.m. - jd 12-22-81

Dwg. 7754A 85

The reaction of Eq. (1) indicates that the net flow of one mole of H_2 into the anode pore produces a net flow of one mole of H_2O and one mole of CO_2 out from the pore. Similarly, the reaction of Eq. (2) indicates that the net flow of one mole of CO into the anode pore produces a net flow of two moles of CO_2 out from the pore. Consequently,

$$\dot{N}_{CO_2} = -\dot{N}_{H_2} - 2\dot{N}_{CO}, \quad \dot{N}_{H_2O} = -\dot{N}_{H_2}$$

Substitution of these relations into Eq. (4) gives

$$Q = \dot{N}_{H_2} [-\mu_{H_2} + \mu_{H_2O} + \mu_{CO_2}] + \dot{N}_{CO} [-\mu_{CO} + 2\mu_{CO_2}] \quad (5)$$

The positive direction for Q is out of the pore.

The gas density ρ_g is related to the universal gas constant R_o , the absolute gas temperature T_g , the gas pressure P , and the summation of products $f_\alpha \mu_\alpha$ of mole fraction times the mass per mole for each of the gas species.

$$\rho_g = \frac{P}{R_o T_g} \sum_\alpha f_\alpha \mu_\alpha \quad (6)$$

Substitution of Eq. (6) and Eq. (5) into Eq. (3) after expressing pore area in terms of an equivalent circular area of radius r gives

$$U_p = \frac{R_o T_g}{P \pi r^2} \cdot \left\{ \frac{\dot{N}_{H_2} [-\mu_{H_2} + \mu_{H_2O} + \mu_{CO_2}] + \dot{N}_{CO} [-\mu_{CO} + 2\mu_{CO_2}]}{\sum_\alpha f_\alpha \mu_\alpha} \right\} \quad (7)$$

Determination of pore flow velocity U_p from Eq. (7) requires evaluations of mole flow rates $\dot{N}_{H_2}$, $\dot{N}_{CO}$ of fuel reactants into the pores which are obtained in the following section.

Fuel Reactant Flow Rates

As indicated earlier, most of the anode current generated is in flooded pores⁽³⁾ and the flooded pore current model⁽⁴⁾ of Wasan, Schmidt, and Baker will be extended to obtain net flow rates $\dot{N}_{H_2}$ and $\dot{N}_{CO}$ of fuel reactants into pores. The result from that model is

$$i_j^\alpha = 4\pi m F D_\alpha C_\alpha \sum_{k=1}^{\infty} \frac{\tanh \lambda_k L_j}{\lambda_k} \quad (8)$$

where $i_j^\alpha \triangleq$ limiting current drawn from pore j due to fuel reactant α
 $m \triangleq$ number of electrons given up per molecule of reactant α utilized.

$F \triangleq$ Faraday's constant.

$D_\alpha \triangleq$ coefficient for diffusion of fuel gas reactant α in the electrolyte.

$C_\alpha \triangleq$ concentration of reactant α in the gas stream.

$L_j \triangleq$ length of pore j .

and λ_k are given by the roots of the equation $J_0(\lambda_k r_j) = 0$, where J_0 is the zero order Bessel function of the first kind and r_j is the radius of pore j .

For the Bessel function roots designated by $\eta_k = \lambda_k r_j$,

$$i_j^\alpha = 4\pi m F D_\alpha C_\alpha r_j \sum_{k=1}^{\infty} \frac{\tanh[\eta_k (L_j/r_j)]}{\eta_k} \quad (9)$$

and for the pore length considered longer than its radius, it can be shown that

$$\tanh [\eta_k (L_j/r_j)] \approx 1, \quad k=1 \text{ to } \infty$$

so that writing Eq. (9) for both fuel reactants H_2 and CO yields

$$\begin{aligned} i_j^{H_2} &= 4\pi m F D_{H_2} C_{H_2} r_j \sum_{k=1}^{\infty} \left(\frac{1}{\eta_k} \right) \\ i_j^{CO} &= 4\pi m F D_{CO} C_{CO} r_j \sum_{k=1}^{\infty} \left(\frac{1}{\eta_k} \right) \end{aligned} \quad (10)$$

The total current i_j drawn from pore j is

$$i_j = i_j^{H_2} + i_j^{CO} \quad (11)$$

and the current i drawn from a local area A is the summation from all the n_p pores which are producing current in that area.

$$i = \sum_{j=1}^{n_p} i_j = 4\pi m F (D_{H_2} C_{H_2} + D_{CO} C_{CO}) \left(\sum_{j=1}^{n_p} r_j \right) \left(\sum_{k=1}^{\infty} \frac{1}{\eta_k} \right) \quad (12)$$

Since the local current density I per unit area is obtained by dividing the the total current produced in area A by that area,

$$I = i/A \quad (13)$$

then from Eq. (12) and (13),

$$I = K (D_{H_2} C_{H_2} + D_{CO} C_{CO}) \quad (14)$$

where $K \triangleq 4\pi m F \left(\sum_{k=1}^{\infty} \frac{1}{\eta_k} \right) M$ (15)

$$M \triangleq \sum_{j=1}^{n_p} r_j / A$$

Now the average cell current density $\bar{I}$ will be computed by integrating the local current density I over the area A_c of the cell.

$$\bar{I} = \frac{1}{A_c} \int_{A_c} I \, dA$$

For parallel fuel flow channels, the local concentration of fuel reactants and consequently the local current density are a function of distance x along the channel from the inlet so that integration of the above equation yields

$$\bar{I} = p_c K (D_{H_2} \bar{C}_{H_2} + D_{CO} \bar{C}_{CO}) \quad (16)$$

where $\bar{C}_\alpha = \frac{1}{L} \int_0^L C_\alpha(x) dx$

For various gas channel/current collector arrangements, not all of the anode surface may be directly exposed to the fuel gas stream and, accordingly, the term p_c is the ratio of the anode area that produces current to the total anode area. Eq. (16) can be solved for K

$$K = \bar{I} / p_c (D_{H_2} \bar{C}_{H_2} + D_{CO} \bar{C}_{CO}) \quad (17)$$

The above relation for K will be later used in the following evaluation of net mole flow rates $\dot{N}_{H_2}$ and $\dot{N}_{CO}$ of fuel reactants into representative pore j. The current generated in a pore for each reactant is not only given by Eq. (10) but also is related to the net mole flow rates of fuel reactants by

$$\begin{aligned} i_j^{H_2} &= mF \dot{N}_{H_2} \\ i_j^{CO} &= mF \dot{N}_{CO} \end{aligned} \quad (18)$$

Equating Eq. (10) to Eq. (18) and using Eq. (15) and Eq. (17) gives

$$\dot{N}_{H_2,j} = \frac{\bar{I}}{mFmp_c} (r_j) \frac{D_{H_2} C_{H_2}}{(D_{H_2} \bar{C}_{H_2} + D_{CO} \bar{C}_{CO})} \quad (19)$$

$$\dot{N}_{CO,j} = \frac{\bar{I}}{mFmp_c} (r_j) \frac{D_{CO} C_{CO}}{(D_{H_2} \bar{C}_{H_2} + D_{CO} \bar{C}_{CO})} \quad (20)$$

Since the diffusion coefficient of a gas in a liquid has been shown⁽⁶⁾ to be approximately inversely proportional to the square root of the molecular weight of the gas,

$$\frac{D_{CO}}{D_{H_2}} \approx \sqrt{\frac{\mu_{H_2}}{\mu_{CO}}} = a \quad (21)$$

Substituting Eq. (21) into Eq. (19) and (20) and defining

$$G \triangleq \frac{\bar{I}}{mMFp_c} \cdot \frac{1}{(\bar{C}_{H_2} + a\bar{C}_{CO})} \quad (22)$$

gives

$$\dot{N}_{H_2j} = r_j G C_{H_2} \quad (23)$$

$$\dot{N}_{COj} = a r_j G C_{CO} \quad (24)$$

Now, the local concentration C_{CO} will be related to the local concentration C_{H_2} . Summation of $\dot{N}_{H_2j}$, $\dot{N}_{COj}$ over all the pores at distance x from the flow channel inlet gives $\dot{C}_{H_2}(x)$ and $\dot{C}_{CO}(x)$, the rates of concentration changes of H_2 and CO at location x .

$$\sum_{j=1}^{n_p} \dot{N}_{H_2j} = \frac{d C_{H_2}(x)}{dt} = \left(\sum_{j=1}^{n_p} r_j \right) G C_{H_2} = M A G C_{H_2}(x) \quad (25)$$

Similarly,

$$\frac{dC_{CO}(x)}{dt} = a M A G C_{CO}(x) \quad (26)$$

Eq. (25) and (26) can be used to show that

$$\frac{dC_{CO}(x)}{C_{CO}(x)} = a \frac{dC_{H_2}(x)}{C_{H_2}(x)} \quad (27)$$

Integration of Eq. (27) using the boundary condition $C_{CO}(0) = C_{CO}^{in}$, $C_{H_2}(0) = C_{H_2}^{in}$, where C_{CO}^{in} , $C_{H_2}^{in}$ are fuel gas inlet concentrations of H_2 and CO , gives

$$C_{CO}(x) = C_{CO}^{in} \left(\frac{C_{H_2}(x)}{C_{H_2}^{in}} \right)^a \quad (28)$$

Eq. (28) allows the evaluation of cell outlet concentrations of fuel reactants H_2 and CO when the overall cell fuel utilization or the utilization of one of these fuel reactants is prescribed.

For a prescribed value of fuel utilization, the relations developed above enable the computation (by using Eq. (7)) of flow velocity U_p exiting a pore of given radius r at cell locations just within the inlet and just before the outlet of the fuel flow channel. Since the concentrations C_{H_2} and C_{CO} of H_2 and CO continually decrease in progressing from the cell fuel channel inlet to exit as the fuel is utilized, Eq. (7), (23), and (24) show that the flow velocity U_p from pores continually decreases from inlet to exit. Consequently, evaluation of Eq. (7) for inlet and exit anode regions bounds the range of pore flow velocities throughout the anode channel length.

The average flow velocity $\bar{U}(x)$ from the anode which was discussed in the last section was derived in a similar manner to that described above

$$\bar{U}(x) = \mu GM(C_{H_2}(x) + aC_{CO}(x))/\rho_g \quad (29)$$

where
$$\begin{aligned} \mu &= -\mu_{H_2} + \mu_{H_2O} + \mu_{CO_2} \\ &= -\mu_{CO} + 2\mu_{CO_2} \end{aligned} \quad (36)$$

The evaluation of pore flow velocities requires the quantification of M defined by Eq. (15). Since this equation does not express M in terms of readily measurable quantities, the Appendix gives a method for evaluating M using porosity data frequently obtained for fuel cell electrodes.

The above relations provide conservative values for flow velocities from pores based on the assumption that all the inlet CO reacts in the pores according to Eq. (2). However, a significant fraction of CO reacts in the anode flow channel with H_2O (produced by Eq. (1)) to produce additional H_2 by the water-gas shift reaction. Due to higher diffusion rates into pores of H_2 compared to CO, the water-gas shift reaction results in somewhat higher flow velocities from pores and greater deposition inhibition at critical downstream anode regions than for the CO utilized exclusively in the pore reaction

Curve 730607-A

Fig. 5 - Pore flow velocity vs. particle settling velocity

R.A. Wenglarz
d.m.s. - jd 12-22-81

Curve 730607-A

given by Eq. (2). Consequently, the following results indicate a lower limit on downstream flow velocities from pores and the tendency of flow from pores to restrict deposition.

Pore Blockage

As indicated earlier, entry into a pore and potential blockage by particles significantly smaller than the pore diameter will be addressed by comparing the particle deposition velocities relative to the gas with average flow velocity exiting the pore. Figure 5 compares particle gravitational settling velocities versus particle diameter to average pore flow velocities versus pore diameter for anode regions at the channel exit where pore flow velocities are lowest. Particle deposition velocities associated with the remaining particle transport mechanisms are not shown since in all cases their values are more than an order of magnitude lower than pore flow velocities and barely extend past the lower limit of the scale and only for particle diameters smaller than about one micron. Furthermore, for these particle diameters, thermophoresis and effects of the average flow velocity from the anode described earlier are expected to greatly reduce and probably prevent particles from approaching the vicinity of pore entrances.

Figure 5 shows that for all particle diameters smaller than pore diameters, flow velocities from pores greatly exceed particle gravitational settling velocities except for particles diameters approaching a few microns. At these particle diameters, the settling velocities approach flow velocities from pores of comparable diameters. The results given in Figure 5 indicate that blockage of flooded pores can be prevented by gas flow from those pores averting particle entry. Because the maximum flooded pore diameter for the fuel cell evaluated was three microns, the flooded pore analytical results cannot be extended to the larger thin film pores. However, due to their larger diameters and lower rates of anode current production, flow velocities from the thin film pores are likely much lower than for the flooded pores so they may be prone to particle entry and blockage. On the other hand, since these larger thin film pores are not the major contributors to molten carbonate fuel cell anode current, it is not clear whether the extent of blockage that may occur results in unacceptable cell performance.

Although the discussion in a previous section indicates that thermophoresis and the average flow velocity from the anode will greatly inhibit and probably eliminate arrival on the anode of particles smaller than about one micron, pore blockage due to particles larger than one micron alighting on the entrances of pores of smaller diameter has not been considered. Determination of particle movement approaching and within a higher velocity "jet" from a pore of comparable or smaller diameter is a complex modeling and analytic effort beyond the intent of this initial assessment of fuel cell deposition.

CONCLUSIONS

An initial theoretical treatment of molten carbonate fuel cell anode deposition has been provided for anode channel regions beyond where flow channel entry effects are significant. Dominant particle transport mechanisms have been identified and relations have been derived for flow velocities from flooded pores which greatly affect anode arrival rates.

Flow velocities from pores decrease in progressing from anode inlet to exit due to depletion of fuel gas reactants. Since flow from anode pores tends to restrict particle arrival on anode surfaces and entry into pores, the potential for deposition continually increases in progressing from channel inlet to exit. At near exit regions of highest potential for deposition, flow from anode pores together with thermophoresis effects may prevent both particle arrival on anode surfaces and particle entry into pores for particle diameters less than about one micron. Particles with diameters greater than one micron do not appear likely to enter flooded pores of somewhat larger diameters but may possibly alight on and block the entrances of pores of significantly smaller diameters. Further theoretical efforts are suggested to determine the pore and particle diameters at which a particle descending toward a relatively smaller pore at a low deposition velocity is repelled by the smaller but relatively higher velocity "jet" issuing from the pore. Other areas for additional theoretical work include analysis of the average descent velocity for larger than one micron particles traversing over a field of "jets" issuing from anode pores of a specified size distribution.

APPENDIX - DETERMINATION OF M

An approximate approach for determining M utilizes the pore size weighting distribution which gives the number $N(r)$ of pores in a size range dr . Then the summation of Eq. (15) can be expressed as

$$M = \sum_{j=1}^{n_p} r_j / A = \frac{1}{A} \int_0^{r_p} N(r) dr \quad (31)$$

The distribution $N(r)$ can be obtained from the fraction $Ra(r)$ of cumulative volume $V(<r)$ of pores with radii less than r divided by the total pore volume which is frequently measured for fuel cell electrodes using Hg- porosimetry.

$$Ra(r) = \frac{V(<r)}{\gamma AT} = \frac{\int_0^r N(y) dV(y)}{\gamma AT} \quad (32)$$

where AT is the anode volume (area A times thickness T), γ is anode porosity and $dV(y)$ is the differential volume of a pore of radius y given for a constant average pore length $\bar{\ell}$ by

$$\begin{aligned} V(y) &= \pi y^2 \bar{\ell} \\ dV(y) &= 2\pi \bar{\ell} y dy \end{aligned} \quad (33)$$

Then substitution of Eq. (33) into Eq. (32),

$$Ra(r) = \frac{2\pi \bar{\ell}}{\gamma AT} \int_0^r N(y) y dy \quad (34)$$

Differentiating both sides and solving for $N(r)$ yields

$$N(r) = \frac{\gamma AT}{2\pi \bar{\ell}} \frac{Ra'(r)}{r} \quad (35)$$

so that substitution of this result into Eq. (31) gives

$$M = \frac{\gamma T}{2\pi \bar{\ell}} \int_0^r \frac{Ra'(r)}{r} dr \quad (36)$$

In pore model analyses, reasonable approximations have been obtained by assuming the pore lengths equal to the electrode thickness (i.e., $\bar{\ell} = T$). Using that approximation in Eq. (36) gives M in terms of commonly measured data for γ , anode porosity, and $Ra(r)$, cumulative pore volume up to radius r over total pore volume.

Experimental and analytical results⁽⁵⁾ indicate that for efficient molten carbonate fuel cell performance only about 5% of anode volume is filled with the electrolyte occupying only the smallest pores which are flooded. Using a cumulative anode pore size distribution⁽¹⁾ $Ra(r)$ (approximated by straight line segments on a log r scale) which has provided excellent molten carbonate fuel cell performance and a value for r of 1.5 microns which results in 5% of total pore volume filled by electrolyte, the following value for M has been obtained,

$$M = 1.45 \times 10^2 / \text{cm} \quad (37)$$

Although the above determination of M depends on the assumption that all pore lengths are equal to the electrode thickness (a questionable assumption which nevertheless has yielded theoretical results in agreement with fuel cell measurements), the value of M given by Eq (37) appears reasonable when compared to an upper bound M_u given by

$$M_u = \sum_{j=1}^n r_j / A \quad (38)$$

where the summation of pore radii is over all n pores in local area A rather than only the flooded pores. The following relation for M_u has been obtained which makes no assumption on the anode pore lengths but only assumes a constant ratio of anode pore area to total anode area at each cross section throughout the depth of the anode.

$$M_u = \gamma \bar{r} / (\bar{r}^2 + s^2) \quad (39)$$

where γ is the anode porosity, and $\bar{r}$, s are the mean particle radius and standard deviation, respectively, of the pore size distribution. For the sharply peaked pore size distributions typical of molten carbonate fuel cell electrodes, the standard deviation s can be neglected without substantial error and using typical values of 70% anode porosity ($\gamma = 0.7$) and five micron average pore diameter ($\bar{r} = 2.5 \times 10^{-4}$ cm) yields

$$\mu = 8.9 \times 10^2 / \text{cm}$$

This value is nearly an order of magnitude higher than the previously calculated value of M which might be expected since the summation of Eq. (38) for μ is over all pore sizes whereas the summation of Eq. (31) for M is only over the smallest pores representing 5% of anode pore volume.

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ACKNOWLEDGEMENTS

This work was funded by the U.S. Department of Energy under the direction of V. P. Kothari. R. E. Kothmann of the Westinghouse R&D Center provided helpful information on fuel cell temperature characteristics necessary for thermophoresis evaluations.