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Estimates for Polarization Losses in Molten Carbonate Fuel Cell Cathodes

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This paper compares the polarization losses associated with the various diffusion-reaction-conduction processes in molten carbonate cathodes. The comparisons are made by estimating each type of loss in terms of component electrochemical potentials in joules/mole; this allows diffusive, charge-transfer, and ohmic losses to all be put on equal footing. For characteristic parameter values, diffusion in both the gas and electrolyte phases and conduction in the electrolyte account for similar polarization losses; charge-transfer and conduction in the solid electrode account for significantly smaller losses. These results tend to support and unify the previous work of numerous investigators. Also molecular-channel interactions are found not to contribute significantly to the polarization loss.

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In recent years, a number of studies have attempted to determine which portion of the overall cathodic process accounts for the majority of polarization losses in molten carbonate fuel cell (MCFC) cathodes. These studies have resulted in a variety of conclusions, some of which may at first glance appear contradictory. Through ac impedance measurements, Yuh and Selman¹ found that charge-transfer accounts for the majority of the overall polarization loss at lower temperatures (600°C), while mass transport (diffusion) and/or slow recombination are more important at higher temperatures (700°C). Their work does not distinguish the roles of gas-phase and electrolyte-phase transport. Prins *et al.*²⁻⁴ also made ac impedance measurements; they concluded that for relatively rich inlet gas concentrations, the polarization losses are dominated by ohmic loss (electrolyte conduction). For lower inlet gas concentrations, electrolyte diffusive transport became more significant.⁴ Fehribach *et al.*⁵ directly computed the current production in a small 100 × 100 μm cathode cross section, and found that on this scale, the diffusive transport in the electrolyte is the greatest contributor to the polarization loss. Kunz and Murphy,⁶ on the other hand, suggest that gas-phase diffusional resistance increases with decreasing inlet gas concentrations and accounts for a significant portion of the polarization loss. Recent work by Peelen *et al.*⁷ found that in particular a carbon dioxide partial pressure below 0.05 atm was detrimental to a MCFC cathode current density of 150 mA/cm².

The present work is a brief, but we hope useful, theoretical estimate of the polarization losses in MCFC cathodes; it supports and reinforces many of the conclusions discussed above, and to some extent, unifies them. The estimates are made using the component electrochemical potentials introduced by Fehribach *et al.*^{5,8,9} This formulation is particularly useful here because it allows the various cathodic processes (diffusion, conduction, electrochemical reactions) to be compared on the same scale (*i.e.*, equal footing). This work differs from our earlier work⁵ in that here we are considering an entire laboratory cathode (800 μm thick) rather than a small cross section, and that now we are making theoretical estimates rather than attempting to compute precisely the current production in the electrode. The general nature of these estimates allows us to consider ranges of parameter values that more or less cover all reasonable values. Thus what is presented here is a direct (if somewhat lengthy) back-of-the-envelope calculation.

This article is divided into two main sections: the first discusses the structure of the MCFC cathode and the electrochemistry which occurs there, the second deals with the estimates themselves. So quantities computed in the first section below are exact given the

assumptions made about the cathode structure and parameter values, while quantities presented in the second section are mainly rough estimates and are therefore more speculative. The values used throughout this article assume that the solid electrode is made of NiO, that the electrolyte is 62/38% Li/K-CO₃, and that the inlet gas partial pressures are between 0.05 and 1. The rate-determining reaction step is also assumed to occur at the electrolyte-solid interface.

Cathodic Structure and Processes

This section describes the MCFC cathode structure and its basic electrochemical processes. The values presented in this section are exact, though sometimes averaged and based on assumed physical parameters. All of the estimates are made in the following section. The component potentials used below are defined in terms of the electrochemical potentials of the various species in a MCFC cathode (*cf.* Ref. 5, 8, 9, 10 for complete details). Because of the assumption that a single rate-determining reaction step occurs at the electrolyte-solid interface, the entire diffusion-reaction-conduction process in the porous cathode can be described in terms of two component potentials, the oxidant potential μ_{ox} and the current potential μ_{c}

$$\mu_{\text{ox}} := \mu_{\text{O}_2} + 2\mu_{\text{CO}_2}$$

$$\mu_{\text{c}} := -4\mu_{\text{e}^-} + 2\mu_{\text{CO}_3^{2-}} \quad [1]$$

Although technically CO₂ is not an oxidant, its role in the overall oxidation process is key, so it is convenient to use the word oxidant to describe the first component and its constituents. The current component is divided into two portions, one in the electrolyte, the other in the solid: $\mu_{\text{ce}} := 2\mu_{\text{CO}_3^{2-}}$, and $\mu_{\text{cs}} := -4\mu_{\text{e}^-}$.

For purposes of this discussion, assume that the cathode thickness is $L = 800 \mu\text{m}$ and that it is composed of three phases: gas channels, electrolyte, and solid electrode. Further assume that the proportions of these phases are 40% gas channels, 20% electrolyte, and 40% solid electrode, and that each of these phases is connected. This last assumption is crucial for transport, but is generally valid for three-dimensional electrodes. Finally assume that the relative percentages of each of the three phases are approximately the same in any cross-sectional cut of the cathode: 40% gas channels, 20% electrolyte, and 40% solid electrode. This final assumption simply implies that the cathode is homogeneous, not having most of a particular phase in a particular part of the cathode. Because the electrolyte accounts for only approximately half of the volume of the other two phases, it is perhaps best to think of this phase as a coating on the solid electrode. This view is consistent with recent scanning electron micrograph (SEM) images.^{11,12}

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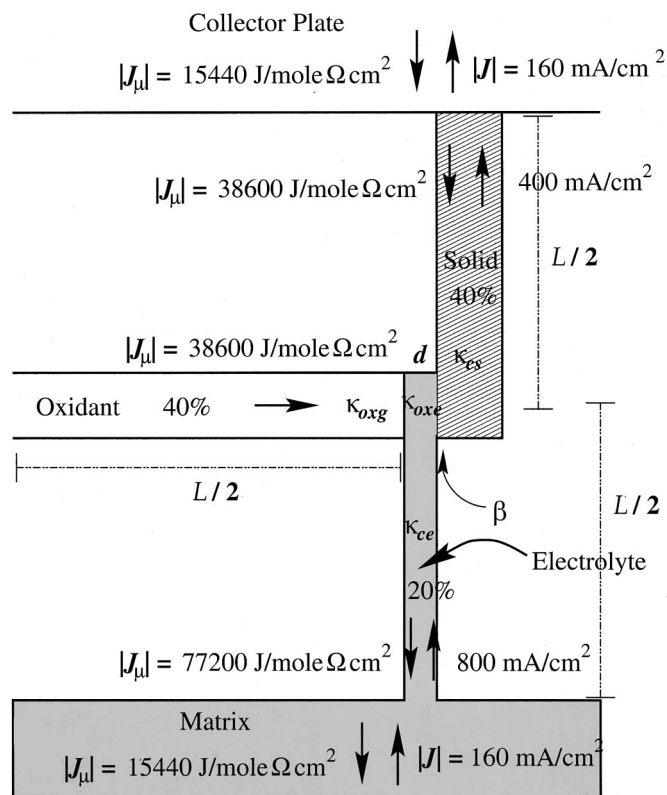


Figure 1. Schematic of a MCFC cathode.

The general description of the MCFC cathodic processes is depicted in Fig. 1. Molecules of the oxidant gases (O_2 and CO_2) enter the cathode and diffuse through the gas channels some distance until they reach some portion of the gas-electrolyte interface. There they cross this interface and diffuse across a presumably thin layer of electrolyte (suppose that the average electrolyte layer thickness is $d = 1 \mu\text{m}$) until they reach the electrolyte-solid interface. Here the rate-determining reaction step occurs: the oxidants combine with electrons which move via conduction through the solid electrode to form excess carbonate ions. For our present purposes, the recombination reaction steps involving the CO_2 may occur either at the electrolyte-solid interface or in the bulk electrolyte, as long as any reaction steps in the bulk electrolyte are fast. This present analysis could be made using the alternate assumption that the recombination reaction is slow and occurs in the bulk electrolyte, but this would lead to a third component (separating the oxidant from the current). For simplicity, this situation is not considered here. The excess carbonate ions move via conduction through the electrolyte, out of the cathode, into the matrix.

The above processes and electrode geometry are obviously so complicated as to make any attempt to describe in detail what happens to each molecule meaningless. One can, however, draw some conclusions regarding what is happening on average. To begin with, assume that the mean value of the current density $|J|$ in both the collector plate and the matrix is 160 mA/cm^2 . This value is typical for MCFC cathodes. Because of the relative proportions of the three phases, the mean current densities in the electrolyte phase near the matrix and the solid phase near the collector are then also determined: $|J| = 800 \text{ mA/cm}^2$ in the electrolyte near the matrix and $|J| = 400 \text{ mA/cm}^2$ in the solid electrode near the collector. Again note that these are mean values, not uniform values; the actual values in certain portions of a given phase will be higher, while in other

portions they will be lower.^c

To complete the description of the cathodic processes, one must incorporate both the reaction step(s) taking place at the electrolyte-solid interface, and the transport of oxidants in the gas phase. Since it is meaningless to discuss a current density $|J|$ (measured in mA/cm^2) in the gas phase, one is forced to look for another quantity which is meaningful in each phase. In terms of the present discussion, this quantity is $|J_\mu|$, the component flux (*i.e.*, the flux associated with the component potential μ). The mean values of this flux entering/leaving each phase is determined in the following three subsections assuming that the mean current density in the matrix and current collector is still 160 mA/cm^2 .

Electrolyte current conduction.—In the electrolyte phase, the component potential for the current μ_{ce} is related to the standard electrical potential ϕ_e by $\mu_{ce} = 2\mu_{CO_3^{2-}} = 2\mu_{CO_3^{2-}}^{eq} - 4F\phi_e$ where $\mu_{CO_3^{2-}}^{eq}$ is the equilibrium potential of the carbonate (assumed to be constant), F is Faraday's constant ($96,500 \text{ C/mol}$), and there are four electrons involved in each net reaction cycle.⁵ Recall that the electrical conductivity σ_e is defined by the relationship $J = -\sigma_e \nabla \phi_e$; a similar relationship defines κ_{ce} , the component (electrochemical) conductivity: $J_\mu = -\kappa_{ce} \nabla \mu_{ce}$. Also since the relationship between the electrochemical potential for the electron and the electrical potential is $\mu_{e^-} = -F\phi_e$, we choose that $J_\mu = -FJ$. Combining these expressions, one finds that $\kappa_{ce} = \sigma_e/4$, implying that κ_{ce} and σ_e have the same physical units. So the mean current-component flux in the matrix is $|J_\mu| = 15,440 \text{ J/(mol } \Omega \text{ cm}^2)$, while in the electrolyte near the matrix $|J_\mu| = 77,200 \text{ J/(mol } \Omega \text{ cm}^2)$. The calculations presented below assume an electrolyte conductivity typical of Li/K carbonate: $\sigma_e = 1.4 (\Omega \text{ cm})^{-1}$ (Ref. 13, p. 2065, and Ref. 14, p. 1643).

Solid electrode current conduction.—The situation in the solid electrode is similar to that in the electrolyte. Here the component potential for the current μ_{cs} is related to the standard electrical potential ϕ_s by $\mu_{cs} = -4\mu_{e^-} = -4\mu_{e^-}^{eq} + 4F\phi_s$ where $\mu_{e^-}^{eq}$ is the (constant) equilibrium potential for the electrons in the solid. The relationships for the conductivities and fluxes in the solid electrode are then as in the electrolyte before: $\kappa_{cs} = \sigma_s/4$, and $J_\mu = -FJ$. So the mean current-component flux in the collector plate is also $|J_\mu| = 15,440 \text{ J/(mol } \Omega \text{ cm}^2)$, while in the solid electrode near the collector plate $|J_\mu| = 38,600 \text{ J/(mol } \Omega \text{ cm}^2)$. The conductivity of the solid electrode is assumed to be a typical value for the cathode material NiO: $\sigma_s = 13 (\Omega \text{ cm})^{-1}$ (Ref. 15, p. 395). Other published values for this conductivity include $\sigma_s = 8 (\Omega \text{ cm})^{-1}$ (Ref. 16, p. 2713) and $\sigma_s = 15 (\Omega \text{ cm})^{-1}$ (Ref. 17, p. 1153, Table I).

Gas-phase oxidant diffusion.—In the gas phase, the component potential for the oxidant is a combination of the chemical component potentials of the two oxidant gases, O_2 and CO_2 : $\mu_{ox} := \mu_{O_2} + 2\mu_{CO_2}$. To compute $|J_\mu|$, the mean oxidant-component flux entering the gas phase, one must again appeal to the overall net reaction balance in the cathode. Because of the stoichiometry of the reaction, there must be a proportionality between the mean current-component flux in the collector plate and the matrix, and the mean oxidant-component flux entering the gas phase. Because of the assumption that the gas and solid phases each make up 40% of any cross section, the mean oxidant flux entering the gas phase must equal the mean current flux entering the solid: $|J_\mu| = 38,600 \text{ J/(mol } \Omega \text{ cm}^2)$.

The final physical characteristic of the cathode that must be determined before computing the estimates of the next section is the specific surface area of electrolyte covering the solid electrode. To

^c These statements about the mean current densities may seem like common sense; mathematically, they are justified by the mean value theorem from basic calculus.

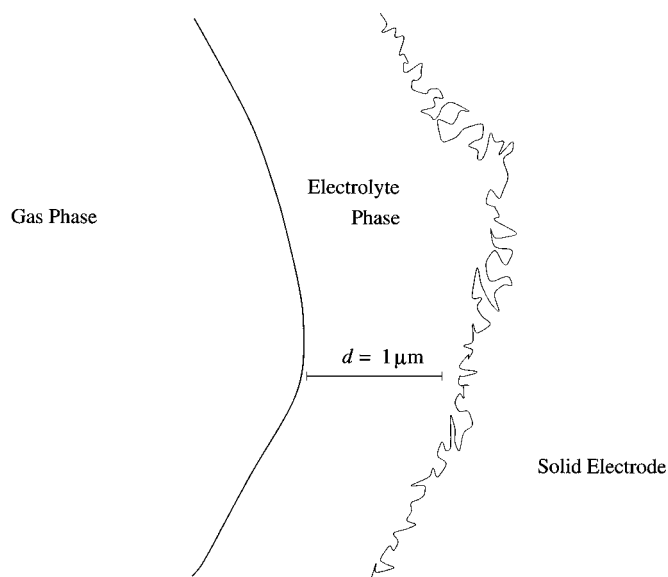


Figure 2. Sketch of the electrolyte layer covering the solid electrode. Note the much greater surface area of the solid electrode than the gas-electrolyte interface due to the roughness (quasi-fractal nature) of the former.

be exact, the surface area discussed here is that of the gas-electrolyte interface, σ_{ge} , and not that of the solid electrode, σ_{es} . The latter is often measured and used in calculations, but tends to yield values for the specific surface area which are too high due to the quasi-fractal nature of the surface of the solid electrode (cf. Fig. 2). For the present discussion, the specific surface area of the gas-electrolyte interface σ_{ge} is assumed to be approximately $700 \text{ cm}^2/\text{cm}^3$. This value is obtained from studying SEM images¹¹ and is approximately one-tenth the measured values for the specific surface area for a solid NiO electrode σ_{es} (cf. Ref. 13, p. 2065, and Ref. 3, p. 1328).

Polarization Estimates

This section presents the estimates themselves. The polarization losses are estimated in terms of the component potential drops across the phases and at the electrolyte-solid interface; hence they are given in units of joules per mole. Each portion of the electrode is again treated separately.

Polarization loss in the solid electrode.—The ohmic polarization loss in the solid electrode can, of course, also be measured in volts as the voltage drop across the solid electrode. The key issue in making this estimate is to describe how much current flows through how much solid electrode. Although much more careful estimates could be made, for present purposes, we assume that a representative value for the current density in the solid electrode is half the value derived in the last section for the current density just under the collector plate. This choice is motivated by the fact that the current density in the solid electrode is decreasing as one moves from the collector plate to the matrix, and is zero in the portion of the solid electrode next to the matrix. So here on-average $|\mathbf{J}| = 200 \text{ mA}/\text{cm}^2$. Since the distance from the collector plate to the matrix (the thickness of the cathode) is taken to be $L = 800 \text{ μm}$, assume that the representative distance l for current flow through the solid electrode is half this value: $l = L/2$. Again this choice is based on the view that as a first approximation, the average distance traversed by the current in the solid is half the cathode thickness. Using these values, and recalling that $\sigma_s = 13 \text{ (}\Omega \text{ cm)}^{-1}$, one can estimate the voltage drop $|\Delta V|$ as

$$|\Delta V| \approx |\nabla \phi_s \cdot l| = \left| \frac{J}{\sigma_s} \cdot l \right| = \frac{L}{2\sigma_s} |J| \approx 0.62 \text{ mV} \quad [2]$$

In Eq. 2 and in the equations below, centered dots (\cdot) indicate multiplication. This voltage drop corresponds to a drop $|\Delta V_\mu|$ in the component potential

$$|\Delta V_\mu| \approx |\nabla \mu_{cs} \cdot l| = \left| \frac{\mathbf{J}_\mu}{\kappa_{cs}} \cdot l \right| = \frac{L}{2\kappa_{cs}} |\mathbf{J}_\mu| \approx 240 \text{ J/mol} \quad [3]$$

Ohmic polarization loss in the electrolyte.—The estimates for ohmic losses in the electrolyte are obtained in the same way as in the solid electrode. The main differences are the smaller electrolyte volume fraction, which implies a higher representative current density, and the lower electrical conductivity. So again $\sigma_e = 1.4 \text{ (}\Omega \text{ cm)}^{-1}$, while our representative current density is now $|\mathbf{J}| = 400 \text{ mA}/\text{cm}^2$. On the other hand, the representative distance that the current flows through the electrolyte is approximately the same as before. So one can estimate the voltage drop $|\Delta V|$ across the electrolyte as

$$|\Delta V| \approx |\nabla \phi_e \cdot l| = \left| \frac{J}{\sigma_e} \cdot l \right| = \frac{L}{2\sigma_e} |J| \approx 11.4 \text{ mV} \quad [4]$$

This voltage drop corresponds to a drop $|\Delta V_\mu|$ in component potential

$$|\Delta V_\mu| \approx |\nabla \mu_{ce} \cdot l| = \left| \frac{J}{\kappa_{ce}} \cdot l \right| = \frac{L}{2\kappa_{ce}} |J| \approx 4400 \text{ J/mol} \quad [5]$$

The above estimates, Eq. 2-5, indicate a significantly higher polarization loss in the electrolyte than in the solid electrode, much as one would expect. Indeed the difference between the estimated values in Eq. 3 and Eq. 5 is large enough to justify, assuming that the solid electrode is a perfect conductor relative to the electrolyte. The estimates below extend this comparison to the other cathodic processes.

Polarization loss in the gas phase.—The estimation of the polarization loss in the gas phase is similar to our first calculations. However, since there is no electrical current in this phase, all of the calculations must be done in terms of component potentials, and therefore one must estimate the component conductivity κ_{oxg} . This conductivity can be computed directly from the diffusivities of O_2 and CO_2 in the gas phase, but because of the relatively low density of the gas phase and the relative smallness of the gas channels, one should consider whether these diffusivities need to be adjusted from their bulk gas values to take into account molecule-channel effects.

One of the standard measures of the importance of molecule-channel effects is the value of D_K , the Knudsen diffusivity.^d For the channel effects to significantly influence the overall diffusivity, D_K must be approximately equal to or smaller than the bulk value (the diffusivities combine by inverse reciprocal addition, as resistors in parallel or in Eq. 7). The bulk gas diffusivity of either O_2 or CO_2 is approximately $1 \text{ cm}^2/\text{s}$ (Ref. 17, p. 1153, Table I).¹⁹ The Knudsen diffusivity is given by $D_K = cd_K/3$ where d_k is the mean diameter of the gas channel, and c is the average molecular velocity

$$c = \sqrt{\frac{8RT}{\pi M}} \quad [6]$$

Here the temperature $T = 923 \text{ K}$, and the molecular mass M for the larger molecule (CO_2) is 28 g/mol . Suppose that $d_k \approx 1 \text{ μm}$; this would seem to be approximately the smallest reasonable choice.

^d See Coppens and Froment¹⁸ for an interesting discussion of this diffusivity and its history.

Using these values, one finds that $c = 83540 \text{ cm/s}$, and thus $D_K \approx 2.8 \text{ cm}^2/\text{s}$. This value for D_K would cause an approximately 30% decrease in the effective diffusivity, relative to the assumed bulk diffusivity of approximately $1 \text{ cm}^2/\text{s}$. While in many cases a 30% change would be significant, here, because we are dealing with order of magnitude calculations, this decrease has no real effect. Also a more realistic (*i.e.*, larger) value for the diameter of the gas channel d_K would result in an even smaller adjustment of approximately 1% or less.

Based on the above calculation, Knudsen diffusivity would not appear to have a significant effect, and the bulk gas diffusivities would seem to be the appropriate ones to use here. The relationship between the oxidant conductivity and the bulk diffusivities for either the gas and electrolyte phases is derived by Fehribach *et al.*¹⁰

$$\kappa_{\text{ox}} = \frac{4F^2}{RT} \left(\frac{1}{D_{\text{O}_2} c_{\text{O}_2}^{\text{eq}}} + \frac{4}{D_{\text{CO}_2} c_{\text{CO}_2}^{\text{eq}}} \right)^{-1} \quad [7]$$

Note that since Eq. 7 applies to both phases, the phase subscript is suppressed. Because in the gas-phase typical equilibrium O_2 and CO_2 concentrations are in the range 5×10^{-7} to $1 \times 10^{-5} \text{ mol/cm}^3$ (5 to 100% gas at 1 atm), the corresponding values of κ_{oxg} are in the range 0.5 to $10 (\Omega \text{ cm})^{-1}$. As was the case in the solid electrode, the representative value of the component flux is taken to be half its value on entering the electrode in the gas phase. So here on average $|\mathbf{J}_\mu| = 19300 \text{ J/(mol } \Omega \text{ cm}^2)$. Since the component potential drop along the gas channels $|\Delta V_\mu|$ is approximately

$$|\Delta V_\mu| \approx |\nabla \mu_{\text{oxg}} \cdot l| = \left| \frac{\mathbf{J}_\mu}{\kappa_{\text{oxg}}} \cdot l \right| = \frac{L}{2\kappa_{\text{oxg}}} |\mathbf{J}_\mu| \quad [8]$$

the calculated range of conductivities implies that

$$77 \text{ J/mol} \leq |\Delta V_\mu| \leq 1500 \text{ J/mol} \quad [9]$$

This calculation suggests that the component potential drop along the gas channels will be fairly low for high O_2 and CO_2 concentrations, but moderately high if either the O_2 or CO_2 concentrations are low.

Diffusive polarization loss in the electrolyte.—The diffusive loss in the electrolyte is estimated in the same way as the diffusive loss in the gas phase. Indeed the short distance ($d = 1 \text{ } \mu\text{m}$) across the electrolyte layer makes this estimate somewhat more accurate, since the component potential will tend to decrease linearly across this layer (the so-called Nernst diffusion). The main difference in this case is the need to appropriately take into account the large specific surface area σ_{ge} of the gas-electrolyte interface. This large value ($\sigma_{\text{ge}} = 700 \text{ cm}^2/\text{cm}^3$) effectively spreads the component flux over the cathode, greatly reducing the component potential drop due to diffusion in the electrolyte. Let A be the cross-sectional area of the cathode; its total volume is then $V = AL$. Since the oxidants which enter the cathode through its gas phase must cross the electrolyte to react at the electrolyte-solid interface, the total quantity of oxidant entering the electrolyte phase must be the same as that entering the gas phase: $|\mathbf{J}_\mu|A$, where $|\mathbf{J}_\mu| = 15,440 \text{ J/(mol } \Omega \text{ cm}^2)$. The total surface area of the electrolyte, on the other hand, is $\sigma_{\text{ge}}V = \sigma_{\text{ge}}A \cdot L$. So the mean component flux is the quotient of the total oxidant to the total surface area

$$\frac{|\mathbf{J}_\mu|A}{\sigma_{\text{ge}}V} = \frac{|\mathbf{J}_\mu|}{\sigma_{\text{ge}}L} \quad [10]$$

The component conductivity associated with diffusion in the electrolyte is again computed using Eq. 7, except that now values for D_{CO_2} , D_{O_2} , $c_{\text{CO}_2}^{\text{eq}}$, and $c_{\text{O}_2}^{\text{eq}}$ typical of the electrolyte must be used. In the electrolyte $D_{\text{CO}_2} \approx D_{\text{O}_2} \approx 1 \times 10^{-5} \text{ cm}^2/\text{s}$, and for 5 to 100% CO_2 at 1 atm, $c_{\text{CO}_2}^{\text{eq}}$ in the electrolyte is in the range 3.5×10^{-7} to

Table I. Comparison of potential/voltage drops. 50% O_2 and 10% CO_2 at 1 atm. Exchange current density, 50 mA/cm^2 . Pseudovoltage drops are given in brackets.

Cathodic process	Component potential drop (J/mol)	Voltage drop (mV)
Solid conduction	240	0.62
Electrolyte conduction	4400	11.4
Gas diffusion	510	[1.3]
Electrolyte diffusion	4700	[12.1]
Charge transfer	22	0.057

$7 \times 10^{-6} \text{ mol/cm}^3$ while for 50% O_2 at 1 atm, $c_{\text{O}_2}^{\text{eq}}$ in the electrolyte is in the range 1×10^{-7} to $1 \times 10^{-6} \text{ mol/cm}^3$ (cf. Ref. 20, p. 1197 and Ref. 21, Table I, with 0.02 mol/cm^3 as the density of molten carbonate). Using these values, one finds that κ_{oxe} is in the range from 2.3×10^{-6} to $3 \times 10^{-5} (\Omega \text{ cm})^{-1}$. The diffusive loss in the electrolyte is then estimated in terms of the component potential drop $|\Delta V_\mu|$ across this layer as

$$|\Delta V_\mu| \approx |\nabla \mu_{\text{oxe}} \cdot d| = \frac{d}{\kappa_{\text{oxe}} \sigma_{\text{ge}} L} |\mathbf{J}_\mu| \quad [11]$$

and based on the parameter values discussed above, one sees that

$$920 \text{ J/mol} \leq |\Delta V_\mu| \leq 12000 \text{ J/mol} \quad [12]$$

Thus, as in the case of diffusion in the gas phase, the importance of electrolyte diffusion to the overall polarization loss depends greatly on the partial pressures of the oxidant gases.

Polarization loss due to charge transfer.—The charge-transfer loss is the loss associated with the rate-determining reaction step at the electrolyte-solid interface. Let β be the inverse reaction resistance; then at the electrolyte-solid interface $\beta |\Delta V_\mu| \approx |\kappa_{\text{oxe}} \nabla \mu_{\text{oxe}}|$.⁵ So, as in the previous case, this loss is estimated as

$$|\Delta V_\mu| \approx \left| \frac{\kappa_{\text{oxe}} \nabla \mu_{\text{oxe}}}{\beta} \right| = \frac{|\mathbf{J}_\mu|}{\beta \sigma_{\text{es}} L} \quad [13]$$

Here the larger value of the specific surface area of the solid electrode should be used (cf. Fig. 2): $\sigma_{\text{es}} = 7,000 \text{ cm}^2/\text{cm}^3$. The value of the inverse reaction resistance β is computed as in Fehribach *et al.*⁵: $\beta := i_0(\alpha_a + \alpha_c)F/RT$. Assuming that the exchange current density i_0 lies in the range from 10 to 100 mA/cm^2 , and that the anodic and cathodic transfer coefficients add up to $2(\alpha_a + \alpha_c = 2)$, one finds that β lies in the range from 0.25 to $2.5 (\Omega \text{ cm}^2)^{-1}$. Since, again all of the oxidants which enter the cathode through its gas phase must react at the electrolyte-solid interface, the mean component flux used here must be $|\mathbf{J}_\mu| = 15,440 \text{ J/(mol } \Omega \text{ cm}^2)$. Using these values, one finds that the component potential drop $|\Delta V_\mu|$ at this interface lies in the range

$$11 \text{ J/mol} \leq |\Delta V_\mu| \leq 110 \text{ J/mol} \quad [14]$$

Notice that this estimate is largely independent of the choice of reaction mechanism. Values in this range would not appear to be significant relative to the larger values computed above.

Conclusions

Our results regarding polarization losses associated with each cathodic process are summarized in Table I. Although one cannot measure electrical potential drops directly in volts for diffusion processes, it is, of course, possible to compute pseudovoltage drops which correspond to the component potential drops in the gas and electrolyte phases. For the calculations presented here these pseudovoltage drops are found simply by dividing the component potential

drops by a factor of $4F$, and are listed in Table I in brackets. The values given in Table I assume a 50% O₂, 10% CO₂ gas mixture at 1 atm, and an exchange current density of 50 mA/cm²; these are typical for MCFC cathodes.³

With reference to the estimates in the previous section and Table I, the main conclusions can be summarized in four points.

1. The size of the polarization loss due to diffusion in both the gas and electrolyte phases depends linearly on the input gas partial pressures. This loss varies in size by a factor of 20 when the gas partial pressures varies from 0.05 to 1 atm, ranging from about one-fifth the value of the ohmic loss (loss due to electrolyte conduction) to several times that value. For the example presented in Table I, most of this loss is associated with electrolyte diffusion, but this conclusion might be reversed if, for example, the gas channels are sufficiently tortuous to increase the representative distance l by a factor of ten. These observations suggest that (i) diffusion and electrolyte conduction will compete for the role of most important in determining the overall polarization loss, and (ii) low gas partial pressures will lead to high diffusive polarization losses, and thus poor cathode performance. This second point is certainly consistent with experimental observations; partial pressures under 0.05 atm are not normally used. Both points are consistent with much of the previous work discussed in the introduction.^{1,4,6,7} In particular, given the physical parameters described above, for high inlet gas concentrations, the dominant polarization loss is the ohmic loss.

2. For any reasonable parameter values, charge-transfer (reaction) losses and ohmic losses in the solid electrode would seem to be significantly smaller, at least compared to ohmic losses in the electrolyte. This suggests that neither improving the conductivity of the solid electrode, nor improving our understanding of the details of the reaction mechanism will significantly reduce polarization losses, unless such improvements are coupled with reductions in the electrolyte ohmic losses. Moving to lower temperatures does increase the significance of the charge-transfer losses, however, not by enough to support the results of Yuh and Selman¹ at 600°C.

3. Reducing the solid-electrode surface area is known to increase polarization losses, and this increase has been attributed to increases in charge-transfer losses. Our calculations suggest that the increase in charge-transfer losses is less significant, but that instead reducing the solid-electrode surface area will increase the polarization loss due to diffusion across the electrolyte, likely making it the dominant loss.

4. Molecular-channel interactions (Knudsen diffusion) would not seem to make a significant contribution to the polarization losses. But this conclusion would change if, for example, the typical gas-channel diameter were significantly less than 1 μm.

All of the back-of-the-envelope calculations presented above, of course, depend greatly on the orders of magnitude of the various physical parameters. If for some reason the value of one or more parameters changes by a significant amount, the conclusions regarding polarization losses could also change. The overall approach used here, however, would still appear applicable for achieving a general understanding of which cathodic processes lead to the greatest polarization losses.

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List of Symbols

A	cross-sectional area, cm ²
c	average molecular velocity, cm/s
d	representative (characteristic) electrolyte thickness, μm
d_K	mean gas-channel diameter, cm
D_x	diffusivity of species X, cm ² /s
D_K	Knudsen diffusivity, cm ² /s
F	Faraday's constant, 96,500 C/mol
i_0	exchange current density, mA/cm ²
J	current density, mA/cm ²
J_μ	component flux, J/(mol Ω cm ²)
l	representative (characteristic) distance, μm
L	cathode thickness, μm
M	molecular mass, g/mol
R	gas constant, 8,314 J/(mol K)
T	temperature, K
V	total cathode volume, cm ³
ΔV	voltage drop, mV
ΔV_μ	component potential drop, joule/mol
Greek	
α_a, α_c	anodic, cathodic transfer coefficients
β	inverse reaction resistance, (Ω cm ²) ⁻¹
$\kappa_{oxg}, \kappa_{oxe}$	oxidant gas, electrolyte conductivity, (Ω cm) ⁻¹
κ_{ce}, κ_{cs}	current electrolyte, solid-electrode conductivity, (Ω cm) ⁻¹
μ_{oxg}, μ_{oxe}	oxidant gas, electrolyte component potential, J/mol
μ_{ce}, μ_{cs}	current electrolyte, solid component potential, J/mol
$\mu_x(\mu_x^{eq})$	(equilibrium) electrochemical potential of species X, J/mol
σ_e, σ_s	electrolyte, solid electrical conductivity, (Ω cm) ⁻¹
σ_{es}, σ_{ge}	electrolyte-solid, gas-electrolyte specific surface area, cm ⁻¹
ϕ_e, ϕ_s	electrolyte, solid electrical potential, mV

Superscripts and subscripts

e	electrolyte phase
g	gas phase
s	solid phase (solid electrode)
eq	equilibrium
ox	oxidant
c	current

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