

SUB-SURFACE CARBON DIOXIDE REACTION IN ANODES

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Abstract

Formation of carbon dust in electrolysis is linked to reaction of the anodes with carbon dioxide. The general understanding is that the reaction takes place inside the anodes, below the bath surface and rather more toward the sides of the anodes than the bottom. Given this, a relevant question is the relative importance of transport through the anode compared to its intrinsic reactivity. To provide quantitative answers, a transport-reaction model has been developed. The key finding is that the extent of reaction is insensitive to the permeability. This is because the reaction produces two moles of CO for every mole of CO₂ consumed, so that there is a net flow away from the reaction locale. Consequently, fresh reactant must be supplied by diffusion rather than convection. Since these two processes are governed by different material properties, this finding opens the possibility of new approaches to optimization of anode structure.

dominant influence on internal mass transport in the sub-surface zone above the working face of the anodes.

This concept, if valid, may have important implications for the interpretation of anode quality measures. A rather simplistic assessment of the situation might be that given sufficient time for the reaction to take place, the gas exiting the anode would be in equilibrium with the carbon, i.e. the reaction would be under mass transport control. Alternatively, if the reaction has not gone to equilibrium, then a change in the intrinsic reaction kinetics will have an important effect on the overall reaction rate. In laboratory anode quality measurement, these two aspects are measured separately: permeability and reactivity are measured independently of each other. It is not clear at first glance which of these might be more important to the behavior of the anodes in the cells. (The reactivity is measured with a test that exposes the outside of an anode sample to a stream of carbon dioxide.) A mistake in interpretation could have serious consequences: if the reaction in the cells is under mass transport control, then a strong focus on the intrinsic or chemical reactivity might be misplaced.

Introduction

Carbon dust in Hall cells is an operational problem in itself, is associated with anode deformations, and is a loss mechanism resulting in increased net carbon consumption. Dust formation is thought to occur due to preferential oxidation of the more reactive pitch coke, allowing for the disintegration of the rest of the anode structure for which the pitch coke forms the glue. The purpose of the present study is a preliminary analysis, using simple models, of several aspects of the reactions leading to dust formation.

Based on observations of industrial anodes, the air-burning reactions are not believed to be strongly responsible for formation of carbon dust. Rather, either the Boudouard reaction or an electrochemical reaction has been determined to be culpable. The focus of the present study is the former:



Near cell operating temperature, the equilibrium of this reaction is far to the right. That is, if there is some carbon dioxide available, most of it will react with any excess carbon to form carbon monoxide.

The initial motivation for the present study was an observation published by Sadler and Algie [1]:

Mass transport of carbon dioxide through the pore structure of anodes will predominantly be via viscous flow and hence related to anode permeability. The driving force for this flow is a hydrostatic pressure of around 200 mm water gauge generated at the electrolytic face of the anode ... This hydrostatic head is likely to be the

In the work cited, Sadler and Algie attempted to remedy this situation by measuring the reaction rate using an apparatus in which carbon dioxide was made to flow through a sample of anode carbon by imposition of a pressure head. As that apparatus is time consuming to operate and so has not been developed into a quality control tool, the desirability remains for some means to link and weight appropriately the contributions of the intrinsic reactivity and anode permeability, particularly under conditions relevant to operating anodes. This attraction was the basis of this study, which started as a model investigation of the reaction situation described in the Sadler quote above.

Our first models in this study were developed on the scale of the anodes, with sizes of the order of half a meter. As will be described, this model did not properly represent the reported effect of the permeability on the amount of internal reaction. Consequently, another effort was made in the development of a model of the Sadler-Algie experiment, which is a time-dependent version of the first model, and on the smaller geometric scale of a few centimeters.

Through the use of these models, an attempt has been made to gain some additional understanding of the corrosion of anodes leading to dust formation. The models are of a preliminary nature, and perhaps will serve to frame and guide additional research in this area.

Finally, an alternative hypothesis has been proposed in the literature to explain carbon dust formation: preferential electrochemical attack of the binder, rather than preferential oxidation by carbon dioxide. This hypothesis was advanced by

Euel Cutshall [2] and found some supporting evidence from Farr-Wharton [3]. For a number of reasons beyond the scope of this paper, the present author is inclined to support the hypothesis of chemical reaction with CO₂ rather than the electrochemical, and additional discussion is limited to the chemical mechanism.

Steady-State Anode Reaction Model

The Model Equations:

This model is based on flow of carbon dioxide, and any carbon monoxide formed, through the anode under the influence of a pressure gradient, simultaneously with their diffusion under a concentration gradients. For each gas, this is modeled with a convection diffusion equation:

$$\nabla \cdot (\bar{u} \cdot [CO_2]) = \nabla \cdot (Deff \cdot \nabla [CO_2]) - R \quad (2)$$

$$\nabla \cdot (\bar{u} \cdot [CO]) = \nabla \cdot (Deff \cdot \nabla [CO]) + 2R \quad (3)$$

The convective velocity is modeled using Darcy's law:

$$\bar{u} = -\frac{K}{\mu} \nabla P \quad (4)$$

The pressure in turn is calculated from the concentrations of the two gases using the ideal gas law:

$$P = ([CO] + [CO_2]) \cdot RT \quad (5)$$

The gas density varies as the gas composition varies throughout the anode. The reaction rate, \mathcal{R} , is modeled as a simple first order reaction:

$$R = k \cdot S \cdot ([CO_2] - [CO_2^{eq}]) \quad (6)$$

The equilibrium constant for equation [1] is about 50 atm. at 950 C. [4]. This means that at 1 atm. total pressure, the reaction will proceed until 98% of the gas phase is CO. As will be seen from the results below, in the reaction zone the CO₂ concentration remains close to the concentration at the surface, so that the neglect of the equilibrium is appropriate for the present level of detail. On the other hand, the kinetics of this reaction are known to follow what is known as the Langmuir-Hinshelwood model in which the reaction is inhibited by both carbon monoxide and carbon dioxide (e.g. [5, 6]). In view of the exploratory nature of this study and the difficulty of finding a suitable set of rate constants for anode materials, this complication has been neglected. However, this may introduce some inaccuracy and should be considered as a topic for further study.

As presently implemented, the effective diffusivity is modeled with no dispersion contribution:

$$Deff = \frac{\varepsilon D}{\tau} \quad (7)$$

The final field equation describes the evolution of the porosity or void fraction:

$$v_{burn} \cdot \frac{d\varepsilon}{dy} = \frac{MWC}{1000 \cdot \rho_{real}} R \quad (8)$$

where the downward anode velocity is given by

$$v_{burn} = j \cdot \frac{MWC}{4 \cdot F \cdot 1000 \cdot \rho_{App}} \quad (9)$$

Equations (2), (3) and (8) comprise the equations for the three field variables in the model with the other equations being the auxiliaries needed for closure. These were solved using the FlexPDE finite element package, generally with no problems.

Parameters, Domain, Boundary Conditions and Solution:

The gas properties: The gas density is from the ideal gas law. The diffusivity is an extrapolation from CO₂ data in CRC Handbook of Chemistry and Physics (85th ed., CRC Press, 2004). (No distinction is made between the diffusivities of CO and CO₂.) The viscosity is uniform, and that of a 50-50 mixture of CO and CO₂. The values of all of the properties are evaluated at 960 C using the formulas given below the list of symbols.

The anode parameters need to include some microstructural information. Generally, the permeability and specific surface area are related, especially for materials with simple structures. The initial intention was to use the Kozeny-Carman relationship, equation (10) between the two to eliminate one parameter from the model. To apply this equation to the anodes, we have considerable permeability data and a few measurements of specific surface area. A typical value of the permeability is 0.5 nPm (nano-perms, equivalent to 10⁻¹³ m²). For the specific surface area, Cutshall reported values in the neighborhood of 1.5 x 10⁶ m²/m³, but some other measurements, particularly of the component coke particles can range higher. Using these values for the surface area and the usual void fraction, it appears that the Kozeny-Carman relationship does not fit well, at least this version of the relationship. This is indicative of a more complex microstructure. Other forms of the equation are available in which the material length scale is provided by a pore or particle size; all of these approaches require a suitable choice of a mean value of the length scale parameter to make the equation work. This might be a fruitful area for further study, but within the present preliminary scope, no additional work was done to relate the permeability to the other properties.

$$K = \frac{196 \cdot \varepsilon^3}{S^2 (1 - \varepsilon)^2} \quad (10)$$

Two parameters are needed in the chemical reaction rate expression, the rate constant and the specific surface area. Rate constants for this reaction have been measured for a variety of types of carbon, however, in view of the scarcity of data related to anode carbons, the use of the simplified first-order kinetics and the present scope, the rate constant has been taken as a variable parameter. Also, without a relationship linking the surface area to the permeability, the surface area only appears in the model when multiplied by the rate constant. Under the circumstances, the product can be taken as a single parameter, which is the

approached used for our first results. By fitting the results to some measured reaction rates, we hope to be able to approximate a suitable value for this joint parameter.

The final microstructural parameter is the tortuosity which appears in the relationship for the effective diffusivity. This parameter relates primarily to the shape of the pores and the sinuosity of the paths that they make for diffusion. A value of three was used for the initial calculations, subsequently allowed to vary.

The apparent and real densities of the anode are set to 1600 and 2100 kg/m³, respectively, which gives a void fraction at the top of the anode of 0.238. The current density, used for the anode disappearance at the bottom, is set to 9000 A/m². Together these parameters give a burn rate or descent velocity of the anode of 1.75 x 10⁻⁷ m/s.

This model has been solved on two geometries. The first corresponds to a one-dimensional column through an anode. The bottom of the anode is immersed 0.12 m into bath of density 2100 kg/m³. Atmospheric pressure is taken as 10⁵ Pa, so that the CO₂ pressure on the bottom of the anode is 102470 Pa. At this surface, the gas is assumed to be 100% CO₂; the concentration is calculated from the ideal gas law. At the top of the 0.60 m thick anode the CO₂ concentration is set to zero and the CO concentration corresponds to 1 atmosphere total pressure. These boundary conditions may not correspond exactly to the physical condition. At a boundary where the gas is flowing outward a different condition may be appropriate, perhaps one with no concentration gradient. However, it is not immediately evident how this should be specified, and for the ranges of the parameters that seem appropriate, the results are relatively insensitive to these boundary conditions.

The second geometry corresponds to an extension of the first to include the corner and side of the anode. The width of the domain is 0.3 m, which, with the plane of symmetry in the center would correspond to an anode of 0.6 m width. The immersed corner of the anode is a circular arc with a radius of 0.04 m. The boundary conditions remain essentially the same: hydrostatic pressure and 100% CO₂ for the immersed parts, and 0% CO₂ and atmospheric pressure for the parts above the bath. Preliminary results with this geometry indicated the possibility of higher extent of reaction than with the 1-D model, and so the model was also extended to include the evolution of permeability and specific surface area.

The specific surface area is assumed to evolve along a parabolic trajectory as a function of the void fraction from its initial specified value through a terminal value of 0.0 when the porosity reaches unity. As the parabola has three coefficients, an additional piece of information is required to complete its specification. For the present, this additional information is the slope of the line fit to the data in Table III of Cutshall and Bullough [8], 1.44E7 m²/m³.

The permeability is assumed to evolve according to an equation of the form:

$$K = \alpha_K \frac{\epsilon^3}{(1 - \epsilon)^2} \quad (11)$$

Results and Discussion:

General Characteristics: A very important feature which is essential to the interpretation of the results is the net volume change associated with the Boudouard reaction: two volumes of CO are produced for each volume of CO₂ reacted. There will be a net volumetric outflow from regions where the reaction is taking place. For the one dimensional model, when the flow resistance of the anode is high enough (thick anode or low permeability), there will be little flow through the anode. Under these circumstances, the reaction will cause a convective flow out of the reaction zone and the reaction is sustained by fresh CO₂ which must diffuse upwind against the convective flow outward. The reaction causes a high pressure zone inside the anode. For a case near the middle of the range of rate constant-surface area and permeability, the maximum pressure is 103760 Pa, it occurs at 0.17 m above the anode bottom, and the flow is outward, both through the bottom and top of the anode, with the superficial velocity equal to -2.E-5 m/s at the bottom and about 1.5E-5 m/s at the top. The porosity increases from the initial value of 0.238 to 0.251 at the bottom. The carbon consumed by this reaction is 1.7% of the electrolytic consumption, in the range of what has been estimated for this reaction. (e.g. 5 to 6% is reported in [7], but that would include the higher extent of reaction on the sides of the anode.)

The sensitivity of this picture to the rate constant-surface area product is shown in Figure 1. Here we see that when the reaction rate is very low, the amount of gas produced is not enough to counterbalance the hydrostatic head imposed by the immersion, and all of the gas flows upward and out the top of the anode. As the rate increases, the maximum pressure becomes linear in the rate constant, and gas escapes from the bottom as well as the top at increasing velocity. Also from this sensitivity analysis, we can get a perspective on the maximum void fraction and the net rate of Boudouard parasitism: with the rate constant-surface area product near 50.E-4 s⁻¹, the void fraction on the bottom face is about 30% and the total fraction reacted is 10-12%. These values indicate the upper limit on the value of the rate constant-surface area parameter that we should consider.

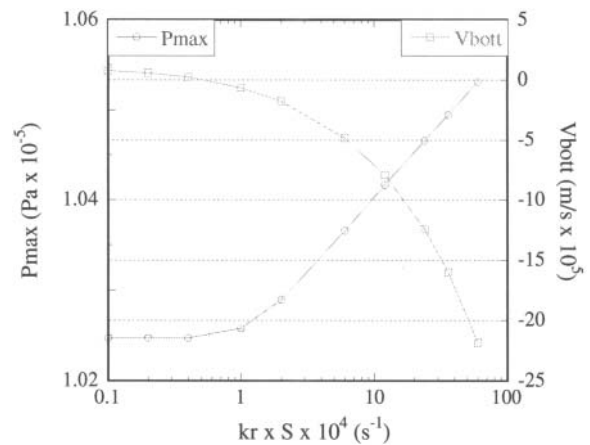


Figure 1: Effect of the rate constant-surface area product on the maximum pressure and superficial velocity at the bottom of the anode.

Effect of Permeability – 1-D Model: The effect of the permeability is a main theme of this paper. The effect calculated

with this model is rather small, which is at variance with the experimental results of Sadler and Algie [1]. Consequently, the question of why the discrepancy needs to be answered. We are placing considerable reliance on the data of Sadler because his experiments were intended to mimic more closely the conditions experienced by the anodes, with the possibility of forced flow of CO₂ through the anode driven by the higher hydrostatic pressure on the working face. This is in contrast to the usual measurement of CO₂ reactivity, wherein a cylindrical sample is exposed on its outside to a stream of the reacting gas. Also, the anodes used by Sadler were made using a simple recipe of multiple size fractions of the same coke and a single pitch, eliminating a range of other influences. Other experimental results, for example Ross, *et al.* [9], which show a correlation between a conventionally measured CO₂ reactivity and permeability, indicate a much lower sensitivity of the reaction rate to the permeability. (This is not entirely a clear comparison, however, as Sadler's experimental conditions and the standard reactivity tests are different.)

Figure 2 shows the effect of the rate constant-surface area product on the maximum pressure inside the anode for two levels of permeability. Similar plots showing the effect on the velocity leaving the bottom of the anode, on the maximum void fraction and on the total reaction rate would show almost no effect of the permeability. Thus we see that changing the permeability does very little except to change the internal pressure in the anode.

At this stage, it might appear that the present results indicate kinetic control, whereas the experiments indicate mass transfer control. With the present model, it would be difficult to change to a mass transfer controlled regime: either the rate constant would have to be increased considerably, or the permeability decreased. The first of these would result in much higher net reaction rates, representing a large fraction of the total carbon consumption, while the second would require permeability much smaller than the measured values. However, a closer look indicates that the diffusive flux is considerably larger than the convective flux, and that discussion of mass transfer control should include the diffusive effects. As a next logical step we examine the geometric effects, moving away from this 1-D representation of a thick anode.

Two-dimensional Results: The evidence linking the formation of carbon dust to the sides of the anodes that are submerged in the bath appears solid. In addition to Cutshall and Farr-Wharton results already mentioned, macrographic examination on anode butts in an earlier work by Sadler and Algie showed deeper extent and more intense attack on the anode sides than on the working face [10]. Figure 3a, 3b and 3c show the pressure, reaction rate and porosity distributions from the model now extended to 2-D. Figures 3b and 3c show that the reaction rate and porosity are higher at the side of the anode than on the working face. This is the expectation, supporting the hypothesis that this mechanism is responsible for the increased formation of carbon dust on the sides of the anode, and perhaps indicating that we are arriving at a quantification of this phenomenon which will allow us to attach a proper weighting to the measured anode properties. However, similarly as the 1-D results, a plot of the integrated reaction rate vs. the reaction rate constant would show overlapping curves for differing values of the permeability. That is, the permeability has very little effect on the reaction rate. On the other hand, Figure 4 shows a marked effect of the tortuosity, here for the maximum void fraction, although the net reaction rate plot is quite similar.

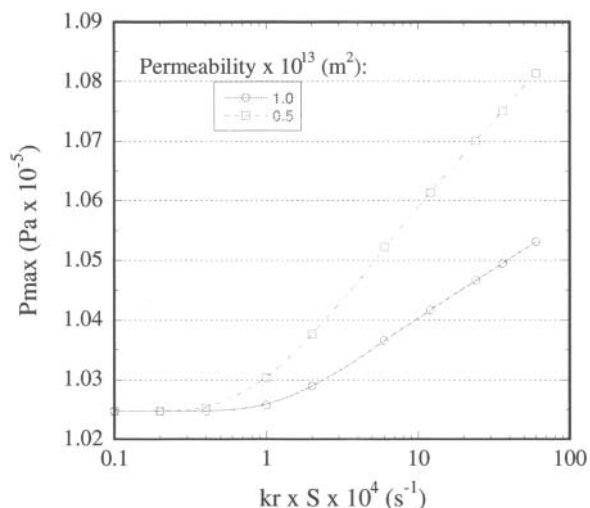


Figure 2: Maximum pressure in the anode vs. rate constant-surface area product for different values of permeability.

So, what we see is that of the two mechanisms for mass transfer, diffusion and convection, the reaction rate depends much more strongly on the parameters that control the diffusion. The tortuosity may or may not be correlated with the permeability, depending on the nature of the microstructure. Some versions of the Kozeny-Carman relationship include it, in which the permeability is inversely proportional to the square of the tortuosity [11]. Generally, it is associated with the distance that material needs to diffuse, or the length of the pore per unit length of the matrix in the flow direction, although other effects such as constrictions can play a role. Tortuosity is generally not measured in anodes. Sufficient data on effective diffusivity of hydrogen is given in a pair of papers by Walker *et al.* [12, 13] to estimate the tortuosity of some carbon materials, which works out to range from 4.5 to 6.8. These are rather large compared to other materials, which more typically are around two and ranging to 4 [14].

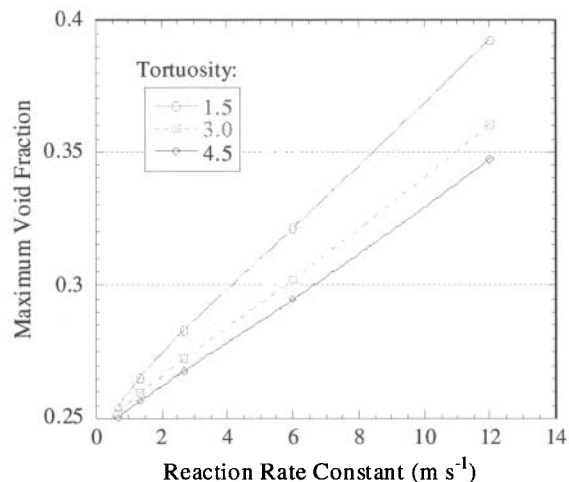


Figure 4: Maximum void fraction vs. reaction rate constant, showing the effect of the tortuosity.

Transient Model – Sadler Experiment

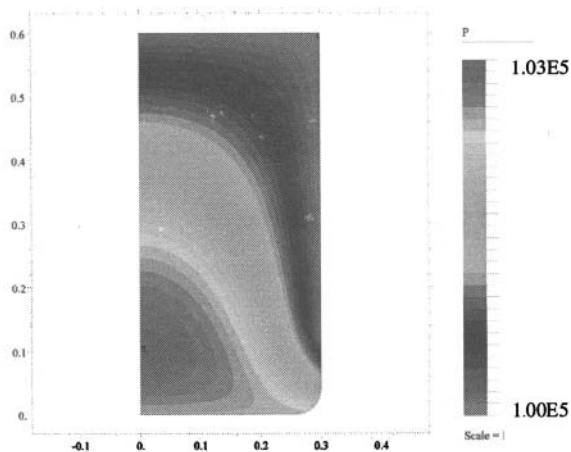


Figure 3a: Pressure distribution for reaction rate constant = 1.33 E-10, $S_0=1.5E6$, $K_0=0.5E-13$ and $\tau=3$.

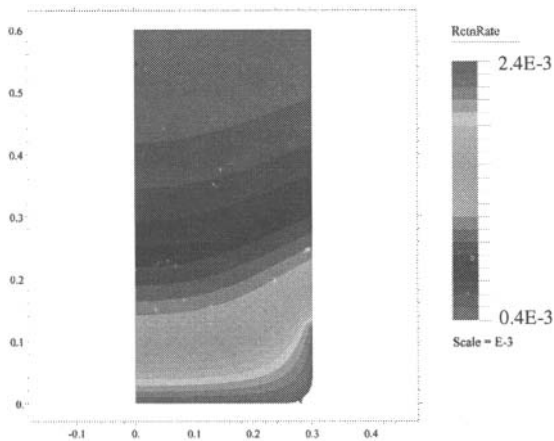


Figure 3b: Reaction rate distribution g-mole/(m³-s); same conditions as Fig 3a.

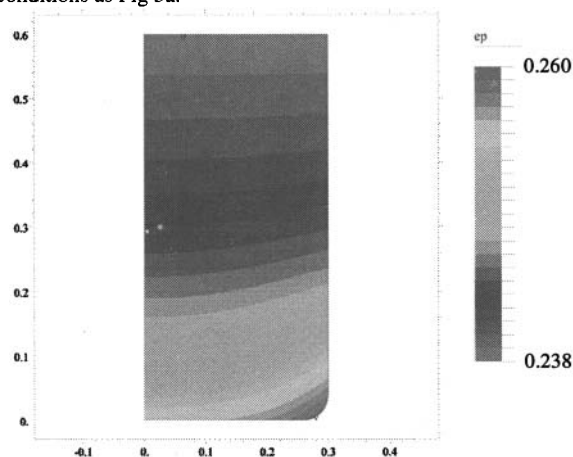


Figure 3c: Void fraction distribution for conditions as Fig.3a.

The above results fit the reports in the literature that carbon dust forms mostly on the sides of the anode below the bath surface. However, Sadler's experimental results show a strong relationship between the anode permeability and the reaction rate, which does not appear in the model results. But since Sadler's experiment was run under different conditions than an operating anode, there is the possibility that some aspect of this difference could be the cause of the differing sensitivity to permeability. Consequently, the model was modified in order to more closely duplicate Sadler's experiment. Transient terms were added to each equation, an additional equation like (2) was added for the argon diluent gas, and the convective term with v_{burn} in (8) was set to zero. The domain boundaries and boundary conditions were modified to fit the samples of Sadler's experiment..

A first model run was completed corresponding to the initial permeability of 6.7 cD, or $0.66 \times 10^{-13} \text{ m}^2$, of Sadler's laboratory anode 2. The initial porosity was calculated from the measured density of 1557. and an assumed real density of 2100. kg/m³. The initial specific surface area was calculated from equation [10] to be $9.66 \times 10^6 \text{ m}^2/\text{m}^3$, based on the specified initial permeability and porosity. The rate constant was adjusted to $33. \times 10^{-10} \text{ m/s}$ to give an overall fraction reacted of 0.1051, which compares with the measured value of 0.103. (from Table 3 of (1)).

Using this value of the rate constant, but adjusting the permeability to correspond to the measured value of Laboratory Anode 1, 15.5 cD, or $1.53 \times 10^{-13} \text{ m}^2$, results in an overall calculated fraction reacted of 0.1056, practically the same as for Anode 2, although the permeability increased by a factor of 2.3. In comparison, the measured fraction converted increased to 0.239, nearly exactly proportional to the increase in permeability. Thus we see that even with the model of the exact experiment, the measured sensitivity to the permeability does not show up in the model results.

Both of these runs used a value of 3.0 for the tortuosity. Decreasing the tortuosity in the second run to 2.0 increased the fraction reacted to 0.112. While this is appreciable, it is not sufficient to account for the difference between the measurements and calculations.

These calculated results are quite similar to those described for the real anode model described above:. Because of the increase in volume due to the reaction, there is generally a convective flow outward from the reaction zone. In order for fresh CO₂ to enter, it must diffuse against this flow. The convective flow itself is relatively insensitive to the permeability; if the permeability decreases, the pressure gradient can increase to provide about the same flow rate, which is ultimately determined by the diffusion rate. Of course, there are secondary effects, which account of for the calculated minor changes due to the permeability.

Summary and Conclusions

The objective was to build a numerical version of a model for sub-surface carboxy reaction in anodes, so that it would be possible to assess the impact of changes in intrinsic reactivity and permeability of the net rate of reaction and the maximum porosity generated. The results are that the model accurately describes the reaction localization on the submerged sides of the anode;

however, there is almost no sensitivity to the permeability. This is at variance with published experimental results, especially those by Sadler and Algie. The reason for the insensitivity is that because of the reaction stoichiometry, there will always be a net flow of gas away from the reaction so that new reactant gas must be supplied by diffusion. The net rate of gas outflow is determined by this upwind diffusion, and the role of the permeability is only to determine the pressure gradient necessary to drive the convective flow. The important parameters that control the mass transfer are those that control the diffusion, namely the porosity and tortuosity. To some extent these are correlated with the permeability, but generally, the functional dependence of the permeability on these parameters are not linear, so that focus on the true parameters rather than the surrogate, permeability, is likely to be a better practice for anode property optimization.

What of the experimental results? We might observe that the samples were fabricated by mixing various size fractions made from the same parent material; this introduces an interesting correlation into the results. The fraction reacted correlates strongly with the permeability, but it correlates just as strongly with the average particle size in the sample. Furthermore, any property that correlates with the particle size would have produced a similar correlation with the extent of reaction. The correlation with the permeability may be happenstance, with the causal variable being something else altogether.

The models described here are very simple, based on homogeneous microstructures. Anodes are more complex, and more accurate modeling will probably depend on taking that into account. Models that include the effects of multiple microstructural length scales exist, such as those describing reactions in beds of catalyst particles. Adaptation of such a model to anodes may be a useful next step.

List of Symbols

D	m ² /s	diffusivity
F	C/eq	Faraday constant
j	A/m ²	current density
K	m ²	permeability
k	m/s	reaction rate constant
MW _x	g/mole	molecular weight of species x
P	Pa	pressure
\mathcal{R}	moles/(s m ³)	chemical reaction rate
S	m ² /m ³	surface area concentration
u	m/s	gas superficial velocity
v_{burn}	m/s	anode consumption velocity
μ	kg/(m s)	viscosity
ρ_g	kg/m ³	gas density
[X]	g-moles/m ³	gas phase concentration of species
X		
ϵ	-	void fraction
ρ_{real}	kg/m ³	real density of the solid
ρ_{App}	kg/m ³	apparent density of the solid
τ	-	tortuosity

Viscosity and Diffusivity Relationships

$$\mu_{CO_2} = (-10.382 + 0.56503 * T - 0.00016364 * T^2) * 1.E-7$$

$$\mu_{CO} = (49.725 + 0.47868 * T - 0.00014113 * T^2) * 1.E-7$$

$$\mu_{mix} = 0.5 * (\mu_{CO_2} + \mu_{CO})$$

$$D_{ab} = 3.6009 * 1.E-9 * T^{3/2} \quad (T \text{ in K})$$

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