Supplementary derivation for:

Effects of an Agglomerate Size Distribution on the PEFC Agglomerate Model

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Below, we consider oxygen transport through the ionomer film surrounding a spherical agglomerate, as depicted in Figure S1. Note, this derivation focuses only on the flux through the ionomer film in order to illustrate the derivation of the correct flux expression to use in the overall agglomerate model derivation of Sun et al. [1].

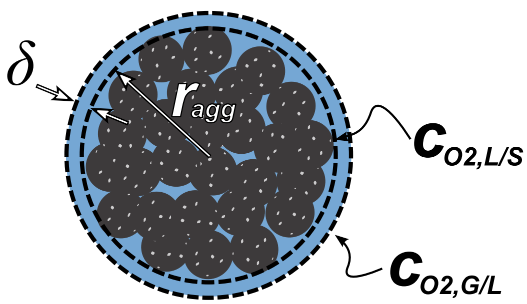

Figure S1: Schematic of a spherical agglomerate.

At steady state, there will not be constant flux along the radial coordinate of the Nafion film. This is because the area changes as we move through the radial coordinate. There will, however, be constant species transport (flux times area, [mol/s]).

Nomenclature	
N_{O2}'	Oxygen flux
c_{O2}	Oxygen concentration
r	Radial coordinate, outward
r_{agg}	Radius of agglomerate not incl. film
δ	Thickness of ionomer film
D	Diffusivity of oxygen through ionomer
B	Constant of integration
Subscripts	
L/S	Interface at $r = r_{agg}$
G/L	Gas/Nafion interface at $r = r_{agg} + \delta$

Flux [mol/m^{2}s] at any point r is given by Fick's law:

$$N_{O2}' = -D\frac{\partial c_{O2}}{\partial r} \tag{S1}$$

The flux at any radius r times the spherical area at that point should be constant:

$$N'_{O2}\left(4\pi r^2\right) = -D\left(4\pi r^2\right)\frac{\partial c_{O2}}{\partial r} = \text{constant} = B_1 \tag{S2}$$

Separate and integrate Eq. (S2):

$$c_{O2} = \left(\frac{B_1}{D4\pi}\right)\frac{1}{r} + B_2 \tag{S3}$$

Apply the following boundary conditions to Eq. (S3):

BC 1: at $r = r_{agg}$ $c_{O2} = c_{L/S}$

BC 2: at $r = r_{agg} + \delta$ $c_{O2} = c_{G/L}$

Using those boundary conditions, solve Eq. (S3) for the constants B_1 and B_2.

$$\begin{aligned} B_1 &= 4\pi D\frac{\left(r_{agg}+\delta\right)r_{agg}}{\delta}\left(c_{L/S} - c_{G/L}\right) \\ B_2 &= C_{L/S} - \frac{B_1}{4\pi D}\frac{1}{r_{agg}} \end{aligned} \tag{S4}$$

Now we return to Eq. (S2) and insert the expression for B_1.

$$-D\frac{\partial c_{O2}}{\partial r} = \frac{\cancel{4\pi} D}{\cancel{4\pi} r^2}\frac{\left(r_{agg}+\delta\right)r_{agg}}{\delta}\left(c_{L/S} - c_{G/L}\right) = D\frac{\left(r_{agg}+\delta\right)r_{agg}}{r^2}\left(\frac{c_{L/S} - c_{G/L}}{\delta}\right) \tag{S5}$$

In the Thiele method, it is the sphere of active material (here, the sphere bounded by the L/S interface, defined by $r = r_{agg}$) that is considered. For this reason, we will evaluate the flux at the L/S interface, and so we apply $r = r_{agg}$. Substituting the expression from (S5) into Eq. (S1), applying $r = r_{agg}$, we obtain $N'_{O2,L/S}$.

$$N'_{O2,L/S} = -D\left.\frac{\partial c_{O2}}{\partial r}\right|_{r=r_{agg}} = D\frac{\left(r_{agg}+\delta\right)r_{agg}}{r_{agg}{}^2}\left(\frac{c_{L/S} - c_{G/L}}{\delta}\right) \tag{S6}$$

Simplifying Eq. (S6), we obtain:

$$N'_{O2,L/S} = D\frac{\left(r_{agg}+\delta\right)}{r_{agg}}\left(\frac{c_{L/S} - c_{G/L}}{\delta}\right) \tag{S7}$$

This is similar to Eq. 8 in Sun et al. [1], except that the fraction $\left(r_{agg}+\delta\right)/r_{agg}$ is inverted.

Using the Eq. (S6) developed here in place of the version in the work by Sun et al. [1], one can follow through the remainder of Sun and coworkers' derivation to obtain the volumetric current density as it stands in Eq. (4) of our paper (note that in applying the Thiele modulus, the pertinent concentration is that at the surface of the active material, i.e. $c_{L/S}$):

$$j_{ORR} = 4F\,\frac{p_{O_2}}{H}\left[\frac{1}{E_r k_c\, f_{agg}} + \frac{r_{agg}\delta}{a_{agg} D(r_{agg}+\delta)}\right]^{-1} \tag{S8}$$

The inverting of the $\left(r_{agg}+\delta\right)/\,r_{agg}$ term has only a minor impact on simulation results, unless the agglomerates are small (order of 100 nm). Some of the agglomerate sizes in the present work are in fact small enough for the effect to be significant, but for the sizes modeled by Sun et al. [1] and many other works, there is little impact on the findings.

Reference:

[1] Sun W, Peppley BA, Karan K. An improved two-dimensional agglomerate cathode model to study the influence of catalyst layer structural parameters. Electrochim Acta. 2005;50:3359-74.