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A new semi-analytical agglomerate model is presented for polymer-electrolyte fuel-cell cathodes. The model uses double-trap kinetics for the oxygen-reduction reaction, which can capture the observed potential-dependent coverage and Tafel-slope changes. An iterative semi-analytical approach is used to obtain reaction rate constants from the double-trap kinetics, oxygen concentration at the agglomerate surface, and overall agglomerate reaction rate. The analytical method can predict reaction rates within 2% of the numerically simulated values for a wide range of oxygen concentrations, overpotentials, and agglomerate sizes, while saving simulation time compared to a fully numerical approach.

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Communication—Modeling Polymer-Electrolyte Fuel-Cell Agglomerates with Double-Trap Kinetics

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A common assumption in the mathematical modeling of polymer-electrolyte fuel-cell (PEFC) cathodes is the existence of small agglomerates, first proposed by Giner and Hunter1 and since then extensively used in literature.2–9 Agglomerate-based models provide a way to incorporate some microstructural details within the macroscale modeling framework necessary for full-cell simulations. The analytical agglomerate models in literature typically assume a first-order Tafel kinetics; however, the literature on oxygen-reduction-reaction (ORR) order is differing.10–12 Furthermore, the coverage of intermediate species is known to be potential and concentration dependent,11,14 resulting in a nonuniform Tafel slope.15 Recently, coverage factors and non-first order kinetics have been incorporated with Tafel kinetics to improve its accuracy;7 however, the model still assumes a single rate-determining step (RDS) and a single Tafel slope.

Double-trap (DT) kinetics13 takes into account multiple reaction pathways and the effect of different species coverages. The model is able to reproduce the doubling of the Tafel slope14 observed experimentally. While Moore, et al.9 used a numerical agglomerate model with different order Tafel kinetics and DT kinetics, only Zenyuk, et al.16 have used a simple analytical approach to include the DT kinetics within an agglomerate model.

This article is aimed at developing an analytical agglomerate model based on DT kinetics, thereby enabling the benefit of both models. The analytical results are compared to a numerical model to access its accuracy.

Theory

Double-trap kinetics.—The cathode ORR is modeled as a dual-pathway reaction13,14

\[
\frac{1}{2} O_2 + H^+ + e^-(RA) \rightarrow OH_{ad} \rightarrow H_2O + H^+ + e^-(RD) \rightarrow H_2O ,
\]  

[1]

\[
\frac{1}{2} O_2 \rightarrow O_{ad} \rightarrow H^+ + e^-(RT) \rightarrow O_{ad} + H^+ + e^-(RD) \rightarrow H_2.
\]  

[2]

Where the steps are RA: reductive adsorption, RD: reductive desorption, DA: dissociative adsorption, and RT: reductive transition. The overall kinetic current is given as the combination of current from the two pathways.

\[
j_{tot} = j^1 e^{-\frac{50G_{RA,KD}^{*}}{2.3RT}} \theta_{OH} - j^1 e^{-\frac{50G_{RD}^{*}}{2.3RT}} \theta_{Pt} .
\]  

[3]

where \( j^1 \) is a reference scaling factor used to set the scale for activation energy with its value set to 1000 mA/cm²; \( \Delta G_{KD}^{*} \) and \( \Delta G_{RD}^{*} \) are the potential dependent energies; and \( \theta_{OH} \) and \( \theta_{Pt} \) are potential and concentration dependent fractional coverage factors of OH_{ad} and free Pt surface respectively. The detailed methodology to obtain these variables is discussed elsewhere in literature.14

Agglomerate numerical model.—A spherical, ionomer-filled agglomerate with a surrounding ionomer film is assumed, with an illustration given in Figure 1. The mathematical model of the agglomerate is similar to the model by Yoon and Weber.7 The agglomerate is assumed to have uniform ionic and electric potential, and the oxygen transport is assumed to be Fickian. The reaction rate in core is calculated using DT kinetics, and no reaction is assumed in the surrounding film. Details of the model are provided in the supplementary material Section 1. From the numerical solution, average reaction rate in core is estimated.

Agglomerate analytical model.—Using a numerical agglomerate model in a complete cathode simulation is computationally expensive. An analytical or semi-analytical model is much preferred. The average reaction rate in the core can be expressed as17

\[
R_{O_2}^{core} = Er_{O_2}^{surf} ,
\]  

[4]

where \( R_{O_2}^{surf} \) is the reaction rate at the surface of agglomerate core (r = r_{agg}). The effectiveness factor \( Er \) is given as18

\[
Er = \frac{1}{\phi_L} \left( \frac{\tanh(3\phi_L)}{3\phi_L} - \frac{1}{3} \right),
\]  

[5]

where \( \phi_L \) is the Thiele modulus. Thiele modulus for a simple m\textsuperscript{th} order reaction, or a Langmuir type of reaction has been provided in

![Image](https://example.com/image.png)

Figure 1. Illustration of an agglomerate and corresponding 1-D computational domain.
literature, however, the DT kinetics does not conform to either of these forms. If the DT kinetics can be approximated with an mth order reaction, the Thiele modulus can be obtained and the equation above used.

### Results and Discussion

**Fitting DT to mth order kinetics.**—The DT reaction rate can be fitted to an mth order Tafel kinetics as follows.

\[
i_{\text{irxn}} = i_0 \left( \frac{c_{O_2}^{\text{ref}}}{c_{O_2}} \right)^m \exp \left( -\frac{\alpha F}{RT} \eta \right)
\]

The reference concentration \(c_{O_2}^{\text{ref}}\) is assumed to be the same as in DT kinetics. Taking the log of Eq. 6 yields

\[
\log i_{\text{irxn}} = m \log c_{O_2}^{\text{ref}} - \frac{\alpha F}{RT} \eta + m \log c_{O_2} = A(\eta) + m \log c_{O_2}
\]

which is linear with respect to \(\log c_{O_2}\). Using Eq. 3, \(i_{\text{irxn}}\) is computed for different overpotential \(\eta\) and oxygen concentration \(c_{O_2}\). Figure 2 shows the plot of \(i_{\text{irxn}}\) against \(c_{O_2}\) at different overpotentials, and its fit to Eq. 6. The Tafel equation results in a good fit to the DT current. The slope of each line is estimated to find the reaction order assumed for further analysis.

The intercept of each fitted line is calculated to get \(A(\eta)\). The term \(m \log c_{O_2}^{\text{ref}}\) is removed from \(A(\eta)\) to eliminate the \(c_{O_2}\) dependence (\(B(\eta) = \log i_0 - \frac{\alpha F}{RT} \eta\)). Figure 3 shows the profile of \(A(\eta)\) and \(B(\eta)\). The slope of \(B(\eta)\) is calculated to obtain \(\alpha\) and the Tafel slope. The intercept of \(B(\eta)\) is calculated to compute the exchange current density, \(i_0\). As expected with DT, two distinct zones are observed with different Tafel slopes and exchange current densities. Table I gives the fitted kinetic parameters for the two Tafel zones.

**Analytical solution for agglomerate reaction rate.**—The mth order fitted equation can be used to estimate Thiele modulus and effectiveness factor. To estimate \(R_{O_2}^{\text{core}}\) from Eq. 4, \(R_{O_2}^{\text{agg}}\) must be known; which is dependent on \(c_{O_2}^{\text{surf}}\), and in turn dependent on \(R_{O_2}^{\text{agg}},\) resulting in an implicit formulation. The following equation can be obtained for oxygen concentration at surface of agglomerate core \((r = r_{agg})\) (see Supplementary Material),

\[
c_{O_2}^{\text{surf}} = \frac{P_{O_2}}{H_{O_2,N}} \left[ \frac{\delta_{agg}^2}{3(r_{agg} + \delta_{agg})D_{O_2,N}} \right] E_k \left( c_{O_2}^{\text{surf}} \right)^{1/2}.
\]

Due to the implicit nature of the equations, the following iterative procedure is designed to obtain surface concentrations and reaction rates:

1. Obtain an initial estimate of rate constant from fitted Tafel kinetics parameters

\[
k_c = \frac{A_4i_0}{4F (1 - \epsilon_s) \bar{V}_{agg}(c_{O_2}^{\text{ref}})^{1/2}} \exp \left( -\frac{\alpha F}{RT} \eta \right),
\]

2. Calculate \(\phi_L\) using the general Thiele equation,

\[
\phi_L = \frac{r_{agg}}{3} \left[ \frac{(1 + m) k_c (c_{O_2}^{\text{surf}})^{m-1}}{2D_{O_2,N}c_{O_2}^{\text{surf}}} \right].
\]

Since \(c_{O_2}^{\text{surf}}\) is not yet known, assume first-order reaction for initial estimate.

**Table I. Fitted Tafel kinetics parameters from DT kinetics.**

<table>
<thead>
<tr>
<th>Variable</th>
<th>Zone 1 ((\eta &lt; -0.4))</th>
<th>Zone 2 ((\eta \geq -0.4))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction order (m)</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Exchange current (i_0)</td>
<td>(5.03 \times 10^{-4} A/m^2)</td>
<td>(1.30 \times 10^{-5} A/m^2)</td>
</tr>
<tr>
<td>Transfer coefficient (\alpha)</td>
<td>0.5</td>
<td>0.96</td>
</tr>
</tbody>
</table>
film thicknesses; high overpotential and larger film thickness results in inaccurate predictions, thereby requiring a third iteration. Large thicknesses and high reaction rates limit the surface concentration.

**Use of DT based agglomerate model for MEA analysis.**—To elucidate the importance of DT kinetics in PEFC simulation, the newly developed semi-analytical model was used in a cathode model of a 2-D cross-section of fuel cell. The cell was modeled in COMSOL using the approach of Zenyuk et al.16 (Details in supplementary section 4). Polarization curves are obtained using the model and compared to polarization curves obtained using Tafel kinetics. Figure 4 shows the comparison of DT and Tafel based polarization curves for a cell which is only limited by kinetic losses and provided with 100% O2 feed. The DT based model has lower current than Tafel due to the lower reaction order. Due to the doubling of slope at higher currents for DT, the difference between DT and Tafel increases at higher currents. For an air feed, similar differences are observed between DT and Tafel (Supplementary material, Figure 5). Overall, it can be seen that choice of kinetics can affect the simulation results. Given that DT kinetics is better representative of experimental data, the new methodology is helpful in using DT kinetics in a cell model.

**Summary**

An iterative procedure was developed to calculate average agglomerate reaction rate using double trap kinetics. An mth order Tafel kinetics was fitted to the DT kinetics. The fitted Tafel parameters and reaction order are used to obtain general Thiele modulus and effectiveness factor, which are used to compute the average agglomerate reaction rate. The reaction rate from the analytical model is within 2% of the numerical results over a wide range of physical and operating parameters. The analytical model enables the use of DT in a full-cell model without being computationally expensive. Cell simulations with DT and Tafel kinetics show difference between the two models, demonstrating the need for an analytical agglomerate model with DT kinetics.

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