EVALUATION OF ELECTRODE PERFORMANCE USING A MICROSTRUCTURE-BASED SIMULATION MODEL

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ABSTRACT

The electrochemical performance of electrodes, such as those used in solid oxide fuel cells, depends to a large extent on the microstructure of the electrode material. A modeling approach, based on the lattice Boltzmann simulation method, has been developed to describe the detailed three-dimensional transport and reaction phenomena occurring in a representative sample of porous electrode material. The model geometry is obtained by obtaining statistical information from a two-dimensional micrograph and reconstructing an equivalent three-dimensional structure. The usefulness of this modeling approach is demonstrated by simulating a simplified two-dimensional electrode.

INTRODUCTION

The electrochemical performance of electrodes, such as those used in solid oxide fuel cells depends to a large extent on the microstructure of the electrode material. The microstructure affects the chemical reaction and species transport characteristics of the electrode in a variety of ways. The diffusion transport of gas species depends in part on the porosity and tortuosity of the gas region. Surface diffusion and oxygen ion diffusion (for mixed conducting materials such as LSF) also depend on the available geometric paths through the structure. The rate of surface chemical reactions also depends on reactive surface availability. For example, anodes using a Ni-YSZ cermet form a triple-phase boundary (TPB) region that may extend some distance away from the electrolyte surface.

The early electrode models consisted of an electrical potential balance that includes terms representing polarization due to diffusion and charge transfer kinetics (1). The kinetics term is generally modeled using an empirical expression, such as the Butler-Volmer equation. The parameters are adjusted to match experimental data. No attempt is made to account for the transport and reaction mechanisms or the electrode microstructure. This approach works well for predicting the performance of a particular electrode under different operating conditions. However, it provides little information on how an electrode with a different microstructure will perform.

More recent electrode models have a specified chemical reaction set applied to simplified representative electrode geometry. The active area is represented by lumped concentration values rather than a distributed field, which washes out the effect of species transport on reaction rates.
Simulation Method

A representative sample of electrode material is subdivided into a large number of lattice sites on an equally spaced Cartesian grid (2). Each site is designated to be either gas or solid with an associated material type. Solid surface sites are identified as well as triple phase boundary intersection sites. Each individual site has an associated temperature, chemical species (gas, surface or solid), potentials, velocity, etc.

Gas flow, such as the net movement of oxygen through the cathode, is determined using the lattice Boltzmann equation, which describes the evolution of the discretized particle distribution function, \( f_i(x,t) \), along direction \( i \) as a function of time. The probability that a particle at location \( x \) has a velocity \( v \) at time \( t \) is given by the distribution function \( f(x,v,t) \). The continuum fields are represented by a finite number of equally spaced lattice points on a Cartesian grid. The velocity field, \( v \), is represented by a finite number of velocity vectors, \( e_i \), connecting adjacent lattice sites, where \( i \) indicates the vector direction. The continuous particle distribution function, \( f(x,v,t) \), is represented by the discretized particle distribution function, \( f_i(x,t) \), which has the same units as density. The lattice displacement vectors for two and three dimensional systems are shown in Figure 1.

The new time distribution function is given by the equation

\[
\left[ f_i(x + \Delta e_i t, t + \Delta t) - f_i(x, t) \right] = -\frac{1}{\tau} \left[ f_i(x, t) - f_{eq}(x, t) \right]
\]

where \( \tau \) is a linear relaxation parameter and \( f_{eq} \) is the local equilibrium distribution. The local equilibrium is expressed in the form of a quadratic expansion of the Maxwellian distribution

\[
f_{eq} = w_0 \left[ A_0 + D_0 u^2 \right]
\]

\[
f_{eq} = w_i \left[ A + B(e_i \cdot u) + C(e_i \cdot u)^2 + Du^2 \right]
\]

where the coefficients are defined as

\[
A_0 = \rho - 6A ; \quad D_0 = -\frac{\rho}{c^2}
\]

\[
A = \frac{\rho}{3c^2} ; \quad B = \frac{\rho}{3c^2} ; \quad C = \frac{\rho}{2c^2} ; \quad D = -\frac{\rho}{6c^2}
\]

and \( c \) is the reference lattice speed, \( c = \Delta x/\Delta t \). The weight coefficients, \( w_i \) for a three-dimensional system are

\[
w_i = \begin{cases} 
\frac{1}{3} & i = 0 \\
\frac{1}{18} & i = 1-6 \\
\frac{1}{36} & i = 7-18 
\end{cases}
\]

The linear relaxation parameter, \( \tau \), is related to the kinematic viscosity by the expression:
\[ v = (t - 0.5)\Delta t/c^3 \]  

Solution method consists of a streaming stage and a collision stage for each time step. During the streaming stage, each lattice site transmits distribution information with adjacent neighbor sites. The incoming information is then relaxed toward an equilibrium distribution, which is determined by local conditions. The new time pressure and velocity values are determined using the expressions

\[ p = \frac{c}{3} \sum_i f_i \]  
\[ \mu = \sum_i f_i e_i \]

This procedure is repeated for the specified number of time steps until a steady-state solution is obtained. The result is a second-order solution to the incompressible Navier-Stokes and continuity equations

\[ \rho \frac{\partial u}{\partial t} + \rho u \cdot \nabla u = -\nabla p + \rho \nabla^2 u \]  
\[ \nabla \cdot (\rho u) = 0 \]

The transport of scalars such as energy or chemical species is calculated using the convection-diffusion equations

Energy -  
\[ \frac{\partial (\rho U)}{\partial t} = \nabla \cdot (k \nabla T) + u \cdot \nabla (\rho U) + Q \]  

Gas species -  
\[ \frac{\partial c}{\partial t} = \nabla \cdot (D \nabla) \mu + u \cdot \nabla c + R \]  

Solid species -  
\[ \frac{\partial c_s}{\partial t} = \nabla \cdot (D \nabla) \mu_s + R_s \]  

Surface species -  
\[ \frac{\partial c_{surf}}{\partial t} = \nabla \cdot (D_{surf} \nabla) \mu_{surf} + R_{surf} \]

Electrical conductance -  
\[ -I_r = \sigma \nabla^2 \phi \]

where \( U \) is internal energy, \( T \) is temperature, \( k \) is thermal conductivity, \( c \) is molar concentration, \( D \) is the diffusion coefficient, \( \mu \) is the chemical potential and \( Q \) and \( R \) are energy and species source terms. The variables in the surface species equation are in terms of surface area rather than volume.

Begin with a passive scalar field that is represented by the variable \( \phi \). The field may be energy, a chemical species or any other passively transported quantity. A scalar distribution function, \( F \), is defined such that:
\[ \varphi(x,t) = \varphi(x,t-\Delta t) + \sum_i F_i(x-\Delta t e_i, t-\Delta t) \]  

which is based on the zeroth moment of the distribution. Note that the distribution function has the same units as the scalar field.

The net transfer of mass from one site to the other can be represented by a new distribution function designated \( f_{\text{conv}} \) that is given by the expression (for direction 1)

\[ f_{\text{conv}} = f^+ - f^- \]

where the plus and minus signs indicate before and after streaming. This variable is the net mass entering the lattice site following streaming from the specified direction. If we assume upwind differencing for the explicit procedure, the convective term for the scalar distribution function at location “a” becomes

\[ F_{l,a} = \frac{\rho_a f_{\text{conv}}}{\rho_a} ; \quad I_{\text{conv}} < 0 \]
\[ F_{r,a} = \frac{\rho_a f_{\text{conv}}}{\rho_a} ; \quad I_{\text{conv}} > 0 \]

The same convection distribution function may be used to calculate the convection transport for all scalar fields.

The diffusion term models the transport of a scalar quantity along the gradient of a specified potential field. The expression used in the lattice Boltzmann method is

\[ F_i = F_i + \Delta t w_i \Delta \varphi D(\varphi_i - \varphi_0) \]

where \( w_i \) are the vector weighting parameters, \( \varphi_i - \varphi_0 \) is the driving potential and \( D \) is the diffusion parameter. The summation for surface species is over a reduced set of adjacent lattice sites in three dimensions using different weighting parameters.

**Chemical Reactions**

The chemical reaction set depends to a large extent on the electrode material. For example, a purely electrically conducting electrode material will experience adsorption reactions and conversion to solid ions only at the triple phase boundary. A mixed conduction material will have significant conversion to solid ions along the surface of the electrode.

**Cathode**

The transport of oxygen is assumed to occur through a number of parallel paths. The initial path is though gas diffusion from the flow channel into the electrode. Surface adsorption may occur, converting oxygen into an adsorbed specie. This form of oxygen may be transported by surface diffusion. Depending on the electrode material, a surface
reaction converts the oxygen into ions, which are then transported by solid diffusion to the electrolyte surface. Gas and surface species diffuse to the triple-phase boundary, where they also are converted to ions.

Surface adsorption: \( O_2 + 2e^- \leftrightarrow 2O_{ads} \) \[21\]

Conversion to solid ion: \( O_{ads}^1 + e^- \leftrightarrow O^2 \) \[22\]

Conversion to solid ion (TPB): \( O_{ads}^1 + e^- \leftrightarrow O^2 \) \[23\]

Transfer to electrolyte: \( O_{electrode}^2 \leftrightarrow O_{electrolyte}^2 \) \[24\]

**Anode**

The oxygen ions are transported from the electrolyte to the electrode surface and is converted into adsorbed surface oxygen. The hydrogen diffuses to the electrode surface, adsorbs onto the surface and reacts with the adsorbed oxygen to form water. Water is released from the surface and diffuses away from the electrode.

Hydrogen adsorption: \( H_2 \leftrightarrow 2H_{ads}^{+1} + 2e^- \) \[25\]

Surface oxygen: \( O^2 \leftrightarrow O_{ads}^1 + e^- \) \[26\]

Combustion (surface hydrogen): \( O_{ads}^1 + 2H_{ads}^{+1} \leftrightarrow H_2O_{ads} \) \[27\]

Combustion (gaseous hydrogen): \( O^2 + H_2(g) \leftrightarrow H_2O_{ads} + 2e^- \) \[28\]

Water desorption: \( H_2O_{ads} \leftrightarrow H_2O(g) \) \[29\]

If greater accuracy is desired for the anode reaction set, equation involving surface OH may also be specified. Each chemical reaction may be solved using either equilibrium or kinetic methods, depending on the relative reaction rates.

**Surface Adsorption/Desorption Reactions**

Surface adsorption/desorption reactions are described using the Langmuir equation. The surface is assumed to have a maximum reaction site density per unit surface area, \( s_{\text{max}} \). The variable \( \theta \) is the fraction of surface coverage, \( s/s_{\text{max}} \). The rates of adsorption and desorption are given by the expressions

\[
R_{ads} = \frac{f(\theta)P}{\sqrt{2\pi nkT}} \exp\left( -\frac{E_{ads}}{RT} \right) = C_{ads}Pf(\theta)\exp\left( -\frac{E_{ads}}{RT} \right) \] \[30\]

\[
R_{des} = C_{des}g(\theta)\exp\left( -\frac{E_{des}}{RT} \right) \] \[31\]

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where $P$ is the gas partial pressure of the adsorbing specie. The function dependence on surface coverage depends on the type of reaction. For simple adsorption/desorption, as in the case of water, the functions $f$ and $g$ have the form

$$f(\theta) = (1 - \theta)$$  \hspace{1cm} [32]  \\
g(\theta) = \theta \hspace{1cm} [33]$$

For dissociative adsorption of a homonuclear diatomic molecule, such as oxygen or hydrogen, the functions are

$$f(\theta) = (1 - \theta)^2$$  \hspace{1cm} [34]  \\
g(\theta) = \theta^2 \hspace{1cm} [35]$$

The net rate of adsorption is given by the expression

$$\frac{ds}{dt} = R_{ads} - R_{des} = C_{ads}Pf(\theta)\exp\left(-\frac{E_{ads}}{RT}\right) - C_{des}g(\theta)\exp\left(-\frac{E_{des}}{RT}\right)$$  \hspace{1cm} [36]$$

Equilibrium is reached when the net rate equals zero. The surface coverage at equilibrium is

$$\theta = \frac{bP}{1 + bP}$$  \hspace{1cm} [37]$$

for simple adsorption and

$$\theta = \frac{\sqrt{bP}}{1 + \sqrt{bP}}$$  \hspace{1cm} [38]$$

for dissociative adsorption, where

$$b = \frac{C_{ads}}{C_{des}} \exp\left(\frac{\Delta E}{RT}\right)$$  \hspace{1cm} [39]$$

**ELECTRODE GEOMETRY MODEL**

Developing a pore scale modeling requires detailed knowledge of the three-dimensional microstructure geometry. The geometry information that is typically available is in the form of two-dimensional micrographs. Therefore, a method was developed for converting a two-dimensional image into an equivalent three-dimensional geometry.

The methodology begins by digitizing a representative portion of a photographic image to obtain an array of grayscale values for each pixel. A computer program was developed to convert this information into a two-dimensional solid map using a filter to remove
artifacts such as light reflections and statistical noise. Statistical information is extracted from the map, including the autocorrelation function and chord length distribution as a function of coordinate direction.

A computer program was developed, based on the simulated annealing technique, to create a three-dimensional geometry with the same statistical characteristics as the two-dimensional picture. The procedure is divided into a coarse grain solution and a fine grain solution. The coarse grain solution begins by randomly distributing spherical particles of the size distribution used to create the electrode structure. A series of Monte Carlo particle moves are attempted by randomly selecting and moving a particle and calculating a merit value for the move based on the change in weighting function that represents the degree of deviation from the target statistical values. This process continues until the improvement in the statistical comparison stops.

The resulting geometry is then subjected to a series of individual solid and fluid node exchanges, which are attempted and accepted based on the same weighting function. The process continues until the statistical values of the model geometry match the target.

The distribution of material and surface types can be treated in a similar manner.

**NUMERICAL EXAMPLES**

The usefulness of this modeling approach is demonstrated by simulating a simplified two-dimensional electrode.

**Two-dimensional Metal Electrode**

A simulation model of periodic rectangular solid metal electrodes on an electrolyte substrate was developed, similar to the geometry shown in Figure 2. This geometry is used to illustrate some of the features of this simulation approach and is not representative of porous metal electrodes. However, Mizusaki et al. (3) and others have created pattern metal electrodes with similar geometries for exploring reaction kinetics and TPB behavior.

This model demonstrates several features of the lattice Boltzmann simulation approach. Gas convection and diffusion transport gaseous oxygen through the pore. The oxygen is adsorbed on the electrode surface and transported to the triple-phase boundary by surface diffusion. The oxygen is then converted into a solid ion at the TPB and transported by solid diffusion through the electrolyte.

The boundary gas is assumed to be at 600°C and have an oxygen partial pressure of 0.1 atm. The total domain has the dimensions of 20x40 microns. The electrode section is 15x30 microns. The resolution is a quarter of a micron.

The electrode surface is assumed to have a maximum reaction site density of $10^{14}$ sites/cm$^2$. The adsorption coefficient is $8 \times 10^{-7}$ RT and the desorption coefficient is $8 \times 10^{2}$, where the oxygen pressure is given in terms of moles/cm$^3$. These coefficients...
result in an equilibrium surface fraction coverage of 0.01. The oxygen surface diffusion coefficient was assumed to be $1 \times 10^{-4}$ cm$^2$/s.

Simulation Results

The system was initialized at inlet conditions and run through a transient until a steady-state condition was reached. The results are presented in Figures 3-5. The variation in oxygen partial pressure is shown in Figure 3. The distribution of the adsorption rate of oxygen on the electrode surface, and hence the effective thickness of the TPB active region, depends to a large extent on the surface diffusion rate. In this case, the adsorption is clustered tightly around the TPB region.

A vector plot of the oxygen current through both the gas and electrolyte regions is shown in Figure 4. Note the high oxygen flux rate through the TPB region. If a mixed conductor was used for the electrode material, additional flux lines indicating oxygen current would appear in the electrode region, coupled with additional flux lines through the electrolyte.

The surface adsorption and disassociation reactions, as well as the reaction at the TPB require a stream of electrons. A vector plot of the electric current through the electrode is shown in Figure 5. Note the concentrated flux near the TPB region as well. The potential is calculated relative to the interconnect boundary condition.

CONCLUSIONS

A modeling approach, based on the lattice Boltzmann simulation method, has been developed to describe the detailed three-dimensional transport and reaction phenomena occurring in a representative sample of porous electrode material. The usefulness of this modeling approach is demonstrated by simulating a simplified two-dimensional electrode. Future plans involve applying this method to a representative three-dimensional electrode geometry and validating by comparing results to experimental data.

REFERENCES

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Figure 1. Lattice displacement vectors for two- and three-dimensional systems.

Figure 2. Description of parallel oxygen transport paths for mixed conducting materials.
Figure 3. Oxygen partial pressure (metal electrode).
Figure 4. Oxygen current in gas and electrolyte regions (metal electrode).
Figure 5. Electrical current (metal electrode).