A MATHEMATICAL MODEL FOR INTERNAL REFORMING AT COMPOSITE ANODES FOR SOLID OXIDE FUEL CELLS

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ABSTRACT

The rate of methane reforming on Ni-YSZ cermet anodes under current load is calculated from a one-dimensional model, including non-linear kinetics, gas-phase diffusion and effects of particle connectivity. The overall rate of the reforming reaction is strongly dependent on anode thickness. However, the current-collector potential at a given current is approximately independent of thickness for thicknesses larger than 10 μm. The ratio between the rates of the reforming and the electrochemical reactions can therefore be controlled within certain limits by optimizing thickness, without significant loss in cell power. Cermet porosity, volume fraction of Ni and Ni-particle size were varied within the constraints set by the requirement of percolation in the gas-phase and the Ni- and YSZ-networks. These parameters appear to have a moderate effect in controlling the rate balance.

INTRODUCTION

Internal reforming of natural gas at the anode of a solid oxide fuel cell (SOFC) (1) to form species more electrochemically active than e. g. methane, is expected to simplify system design and to improve the thermodynamic efficiency of the cell with respect to operation on externally reformed gas (2). The overall amount of electrochemically produced heat is more than enough to balance the overall energy required for the endothermic reforming reaction (3). However, unless the reforming and electrochemical reactions occur at comparable rates locally, large temperature gradients in the cell may result (3-6), which in turn may give rise to intolerable mechanical stresses (6).

In order to facilitate the design of electrode structures capable of balancing the rates of the reforming and electrochemical reactions to any desired degree, we develop here a mathematical model for internal reforming at an SOFC anode with concurrent electrochemical reaction. Our purpose is to demonstrate that significant reduction in the

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ratio between total reforming rate and the rate of electrochemical reactions, $\chi$, may be achieved with negligible loss in overpotential by optimizing cermet thickness, and to discuss other, microstructural means to the same end. Since state-of-the-art SOFC anodes are composites, usually containing Ni- and YSZ (1), we take departure in a recently published model for such electrodes in which aspects of particle-particle connectivity particular to these electrodes are taken into account (7).

MODEL

We consider a porous composite electrode consisting of dense grains of an electronic conductor (‘electrode particles’) and of an ion conductor (‘electrolyte particles’) packed together and interfaced to a dense bulk electrolyte of the same type as the electrolyte particles in the composite at one end, and to a porous current collector at the other (7-9), Figure 1. A gas mixture of hydrogen, methane, water vapour, carbon monoxide and carbon dioxide is led past the electrode at constant flow rate and at a total pressure of $p^0=1$ atm. The gas mixture results from pre-reforming of methane with steam

$$\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2 \quad [1]$$

at an initial steam-to-carbon ratio $S/C$, and a subsequent shift reaction

$$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad [2]$$

The pre-reforming is allowed to proceed until a given fraction $\Delta_i$ of the methane initially present has reacted according to Eq. [1], before the exposure to the composite anode.

A steady-state current is passed through the electrode. We want to calculate the distribution of partial pressures and rates of chemical and electrochemical reactions within the electrode, as functions of current and inlet gas composition. To assess the effect of a change in anode thickness or a microstructural parameter on power loss of the fuel cell, we also want to calculate the potential at the current collector relative to that in the bulk electrolyte close to its interface to the anode. We make the following assumptions: 1) The electrode and electrolyte particles are mixed at random, forming different types of clusters of one type of particles (7-9). 2) Macroscopic, one-dimensional theory for porous electrodes, adapted to take into account effects of connectivity of particle clusters (7), is applicable. This implies that the electrode under test is small enough that there are no gradients in the transverse directions in partial pressures, temperature etc. 3) The volume fraction of metal in the composite is in the range where the polarization behaviour of the electrode is dominated by interfaces between percolating clusters of electrolyte- and electrode-particle clusters (7). 4)
Reactant and product gases are transported through voids left between the particles, and no portions of the composite are sufficiently dense that this gas-phase transport is blocked. 5) All gases behave according to the ideal gas law. 6) Gas-phase transport is adequately treated by Fick's law of diffusion with constant diffusion coefficients (10). The gas flow-rate is sufficiently high that no partial pressure outside the anode is influenced by the reactions occurring inside the anode. 7) The electrode material in the anode catalyses reactions [1] and [2], whereas the current-collector and the electrolyte are catalytically inactive for reforming and shift. 8) The shift reaction is always at equilibrium. 9) The rate of electrochemical oxidation of species other than H₂ is at the partial pressures under operating conditions negligible relative to that of hydrogen (11). The polarization resistance for a contact between an electrode and electrolyte particle is inversely proportional to the three-phase boundary between the gas-phase and the two solid phases, $l_{TPB}$, see References in Refs. (7-9). The reaction proceeds according to

$$H_2 + O^+_O = H_2O + V^-_O + 2e'$$  \[3\]

where $O^+_O$ and $V^-_O$ are (in Kröger-Vink notation) an oxygen atom and an oxygen vacancy in the YSZ lattice, respectively. $e'$ is an electron picked up by the current collector. 10) The electrocatalytic properties of the electrode-electrolyte interfaces in the composite and its catalytic activity for steam-reforming are independent of one another (11). That is, we assume all rate constants to be independent of partial pressures. Gas-phase reactions do not proceed at any significant rate. 11) The anode operates isothermally. 12) Local variations in the open-circuit potential are negligible.

Under the assumptions above, we may write for the current density, $i_{ed}$, flowing through the electrode cluster and the current density, $i_{el}$, flowing through the electrolyte cluster (7)

$$i_{ed} = -\kappa_{ed}^* \varphi_{ed}/dx$$  \[4\]

$$i_{el} = -\kappa_{el}^* \varphi_{el}/dx$$  \[5\]

and

$$di_{ed}/dx + di_{el}/dx = 0$$  \[6\]

where $\varphi_{ed}$ and $\varphi_{el}$ are the potentials in the electrode and electrolyte clusters. (The current densities $i_{ed}$ and $i_{el}$ are averages over the entire cross-sectional area of the electrode.) The clusters have effective conductivities $\kappa_{ed}^*$ and $\kappa_{el}^*$, and the two first relations are expressions for Ohm's law. The last relation expresses charge conservation. For the current transferred from an (percolating) electrode cluster to an (percolating) electrolyte cluster, we write (12,13)
\[ \frac{di_0}{dx} = \lambda_{TPB} i_0 [\exp(\beta_a \eta_a) - \exp(-\beta_c \eta_c)] \]  

[7]

where \( \eta_a = \varphi_{el} - \varphi_{el} - U' \) (U' is the open-circuit potential), and the parameters \( \beta_a \) and \( \beta_c \) have the units of reciprocal potential. In Eq. [7], \( i_0 \) plays the role of an exchange current density given with respect to TPB length, in view of assumption 9). Thus, \( \lambda_{TPB} \) is the three-phase boundary per volume in the anode. We take \( i_0 \) to depend on the partial pressures of hydrogen and water as

\[ i_0 = \left( \frac{p_2}{p_2^o} \right)^{\gamma_2} \left( \frac{p_4}{p_4^o} \right)^{\gamma_4} i_0(p_2, p_4) \]  

[8]

where \( p_2 \) and \( p_4 \) are the partial pressures of water vapour and hydrogen, respectively, and \( p_2^o \) and \( p_4^o \) are reference pressures. (We assign for the following subscript \( i = 1 \) to CH\(_4\), \( i = 2 \) to H\(_2\)O, \( i = 3 \) to CO, \( i = 4 \) to H\(_2\), and \( i = 5 \) to CO\(_2\), following their order of appearance in Equations [1] and [2] above.) The parameters \( \gamma_2 \) and \( \gamma_4 \) are apparent reaction orders with respect to the partial pressures of water vapour and hydrogen, respectively.

For all species, the material balance reads at steady state and in one dimension,

\[ -\frac{dN_i}{dx} + R_i = 0 \]  

[9]

where \( N_i \) is the molar flux of species \( i \) relative to stationary coordinates and averaged over the entire cross-section of the electrode, and \( R_i \) is the rate of production (in mol cm\(^{-3}\) s\(^{-1}\)) of species \( i \) in chemical and electrochemical reactions. According to assumptions 5) and 6) above,

\[ N_i = \frac{D'_i \partial p_i}{RT \partial x} \]  

[10]

where \( R \) is the gas constant, \( T \) the temperature, \( p_i \) the partial pressure of species \( i \), and \( D'_i \) the effective diffusion coefficient of species \( i \) in the gas mixture in the pores of the composite anode (10). Denoting the rate of reactions [1] and [2] \( r_1 \) and \( r_2 \), respectively, both normalized with respect to surface area of catalyst (electrode material) (mol cm\(^{-2}\) s\(^{-1}\)), we may write

\[ R_i = -ar_i \]  

[11]
\[ R_2 = -ar_I - ar_{II} + \frac{1}{2F} \frac{di_{el}}{dx} \]  
\[ R_3 = ar_I - ar_{II} \]  
\[ R_4 = 3ar_I + ar_{II} - \frac{1}{2F} \frac{di_{el}}{dx} \]  
\[ R_5 = ar_{II} \]  

where \( a \) is the surface area of electrode particles per volume in the anode (cm\(^2\)). The last terms in Equations [12] and [14] are production of water and consumption of hydrogen, respectively, due to reaction [3] above. For the rate of the reforming reaction [1], we will use [2]

\[ r_I = k \left( \frac{P_1}{P_3P_4} - \frac{P_3P_4}{K_I P_2} \right) \]  

where \( k \) is a rate constant (mol cm\(^2\) s\(^{-1}\) atm\(^{-1}\)) and \( K_I \) is the equilibrium constant for reaction [1]. From assumption 8),

\[ p_2 = \frac{K_{II}P_2P_3}{P_4} \]  

where \( K_{II} \) is the equilibrium constant for the shift reaction [2].

Sufficient boundary conditions for the coupled equations (4) through (17) are given by

\[ i_{el} = -I, \quad i_{ed} = 0, \quad \varphi_{el} = 0, \quad N_i = 0 \text{ at } x = 0 \]  

and

\[ i_{el} = 0, \quad p_i = p_i^* \text{ at } x = L \]  

where \( L \) is the thickness of the composite electrode and \( x=0 \) corresponds to the interface between the composite anode and the bulk electrolyte (7,13). \( I \) is the superficial current density, and \( p_i^* \) is the partial pressure of species \( i \) at \( x=L \).
Equations [4] through [17] can be combined into a set of six nonlinear equations. Three of these are differential equations, and constitute a well-defined problem once the parameters and cell current are specified. The equations are solved by linearizing around a trial solution, and the resulting linear equations are solved by Newman’s BAND subroutine, as outlined in Ref. (14). The calculations are then repeated using the solution obtained as the new trial solution, until convergence.

In order to calculate the measured current-collector potential, \( \varphi_{el}(x=L) \), from \( \eta_s \), we need to evaluate \( \varphi_{el}(x=L) \). A second-order differential equation for \( \varphi_{el}(x) \) can be obtained by differentiating Eq. [5], replacing \( \frac{d}{dx} \) with the expression given in Eq. [7], and solving the resulting equation in \( \varphi_{el} \) using the results for \( \eta_s \), \( p_z \) and \( p_t \) found above. Boundary conditions are implicitly given by Equations [5], [6], [18], and [19]. This equation is also conveniently solved using the BAND-routine. \( \varphi_{el}(x=L) \) is finally found as \( \eta_s \cdot \varphi_{el}(x=L) \).

**ESTIMATION OF CONSTANT PARAMETERS**

Diffusion coefficients \( D_f \) were evaluated using the formulas given in Ref. (10) from binary diffusion coefficients in Ref. (15) extrapolated to 1000 °C (16). For the effective conductivities \( \kappa_{el} \) and \( \kappa_{el}^* \) above we will use formulas in Ref. (7), based on bulk conductivities of Ni and YSZ at 1000 °C, volume fractions of these and percolation thresholds evaluated from the theory of Bouvard and Lange (17). Porosity \( \varepsilon \) was either 0.3 or 0.04. Specific surface areas, \( a \), are estimated from the particle density in the composite, see Ref. (7). Taking the particle areas to be those of spheres for the cases with porosity \( \varepsilon = 0.3 \), this gives \( a = 9 \cdot 10^3 \text{ cm}^{-1} \). For porosity \( \varepsilon = 0.04 \), this was reduced to \( 3 \cdot 10^3 \text{ cm}^{-1} \) due to the larger necks between particles and consequently lower areas of surface-gas interfaces. The pore radii for calculating Knudsen diffusion-coefficients (10) were estimated to be 0.5 \( \mu \text{m} \) and 0.02 \( \mu \text{m} \) from throats left between particles (18), for the cases \( \varepsilon = 0.3 \) and \( \varepsilon = 0.04 \), respectively. All circumferences of particle necks were set equal to three times the particle radius for contacts between particles of the same kind, and \( l_{pp} \) was set equal to three times the particle radius of the smaller particle (7). Equilibrium constants for reactions [1] and [2] can be found in Ref. (19). The apparent specific exchange-current \( i_0(p_{H_2}^0=0.97 \text{ atm}, p_{H_2O}^0=0.03 \text{ atm}) \) has been estimated from a specific polarization conductances \( \kappa_p \) of \( 1 \cdot 10^4 \text{ S cm}^{-1} \) (7, and references therein) by assuming that the relation \( \kappa_p = i_d(\beta_1+\beta_2) \) holds (12). There appears to be no agreement in the literature concerning apparent reaction orders with respect to water and hydrogen, but \( i_0 \) appears to be less sensitive towards the pressure of the latter than towards the water-vapour pressure, and we will use \( \gamma_2=1 \) and \( \gamma_4=0 \) (20,21-23).

Using a Ni-particle radius of 1 \( \mu \text{m} \) and in addition assuming a porosity of 35\%, the preexponential of the rate constant, \( k_0 \), for the reforming reaction in Achenbach and
Riensche (2) for Ni-YSZ cerments with 20 wt% Ni may be converted to $5 \times 10^5$ mol s$^{-1}$ cm$^2$ atm$^{-1}$. The activation energy is 82 kJ mol$^{-1}$, giving $k = 2.2 \times 10^6$ mol s$^{-1}$ cm$^2$ atm$^{-1}$ at 1000 °C, in reasonable agreement with similar estimates from data in Ref. (5). For our present purposes, we will use the value of $1 \times 10^5$ mol s$^{-1}$ cm$^2$ atm$^{-1}$ for $k$.

RESULTS AND DISCUSSION

In Figure 2 is shown variations in the ratio between the rate of the reforming and electrochemical reactions, $x$, with $L$ for several parameter sets. Curve 1 corresponds to a parameter set with volume-fraction of Ni, $\Phi$, equal to 0.5, porosity $\epsilon=0.3$, and all particle radii equal to 1 µm. In curve 2, $\Phi$ has been reduced to 0.4. In curve 3 of Fig. 2 is demonstrated the effect of reducing the porosity to 4%. In curve 4 of Fig. 2, the radius $a_{en}$ of the electrode particles has been increased to 2 µm with the radius of electrolyte particle $a_{el}$ still equal to 1 µm, which reduces the specific surface area by a factor of 2 with respect to parameter set 1. While the curves 1 through 4 are calculated using $\Delta_{i}=0.05$, curve 5 demonstrates the effect of partial pressures at $x=L$ on the $x$ v. $L$ curve for the same parameter set as in curve 1 by increasing $\Delta_{i}$ to 0.5. In Fig. 2, all curves except the low-porosity case appear to be almost linear, indicating negligible limitations due to mass transfer. This was also confirmed by a quite weak dependence of partial pressures with $x$ for given $L$ ($L=50$ µm) in these cases. For the parameter set corresponding to curve 3, however, we found relatively strong variations in partial pressures with $x$ for $L=50$ µm. All results were consistent with the assumptions made, as far as this was possible to check.

While thickness is crucial for $x$, the effect of the volume fraction of Ni, of the electrode-particle size, and of porosity is more moderate, c.f. Fig. 2. (Although the porosity may appear to be significant in reducing $x$, a porosity of $\epsilon=0.04$ must be considered quite extreme in the present context, and possibly not obtainable in practice in a well-controlled manner.) Figure 3 shows the current-collector potentials as a function of $L$ for the same parameter sets as in Fig. 2. Although $x$ is a strong function of anode thickness, Fig. 2, the current-collector potential for none of the cases indicate significant power loss for thicknesses larger than roughly 10 µm, Fig. 3. Beyond this threshold the potential is not very thickness dependent, although an increase with $L$ for large $L$ in the case with 4% porosity is apparent.

The potentials shown in Fig. 3 may appear to be very low for all cases, and one should note that their values depend crucially on parameters to which significant uncertainty is attached (24). However, we believe that the thickness dependence of the current-collector potential is under the present assumptions still well described by Fig. 3.
CONCLUSIONS

The parameter most important in controlling the ratio of the rate of methane reforming to that of the electrochemical oxidation of the reforming-reaction products at Ni-YSZ cermet anodes, appears to be anode thickness. Manipulating particle size, volume fraction of Ni and porosity would be less effective in balancing the reaction rates. It appears difficult to reduce $\chi$ to values close to one with the presently used Ni-YSZ cermets. Unless porosity gets significantly lower than 30 %, limitations due to mass transfer in these electrodes are not important.

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Fig. 1. Schematic view of a composite electrode. Electrode clusters are shown, whereas electrolyte clusters are indicated as the blank areas. A porous current collector is attached at $x=L$, and the interface to the bulk electrolyte is situated at $x=0$. 
Fig. 2. Ratio $\chi$ of total rate of the reforming reaction to rate of electrochemical reaction v. thickness $L$, for $I=80$ mA cm$^{-2}$. 1) Standard parameters, 2) $\Phi=0.4$, 3) $\varepsilon=0.04$, 4) $a_{\text{cd}}=2$ $\mu$m, $a_{\text{c}}=1$ $\mu$m, and 5) $\Lambda_{r}=0.5$.

Fig. 3. Potential at the current collector, $\varphi_{\text{ed}}(L)$, v. electrode thickness $L$ for the same parameters as in Fig. 2.