Elementary Reaction Models for CO Electrochemical Oxidation on an Ni/YSZ Patterned Anode

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1. Introduction

Solid oxide fuel cells (SOFCs) are known for their fuel flexibility and tolerance to carbon monoxide, CO. Thus, syngas can be used in an SOFC directly in generating electricity. Syngas, a mixture of carbon monoxide, CO, and hydrogen, H₂, is derived from steam reforming of coal, biomass, methane, or other hydrocarbons. In order to optimize the anode performance, it is important to construct comprehensive electrochemical oxidation models H₂ and CO near the three-phase boundary (TPB) of the SOFC, based on sound experimental data and kinetic mechanisms. Compared with the systematic experimental and theoretical studies of H₂ electrochemical oxidation [1,3,4,5,6,7,8,9,10], few studies have been performed for the CO electrochemical oxidation mechanism.

Different reaction mechanisms have been proposed for CO electrochemical oxidation, depending on the experimental conditions and the cell material. To reduce the effects of gas-phase mass transport on the impedance, and eliminate some of the ambiguities in the analysis of electrochemical oxidation rates, Habibzadeh et al. [11] studied the CO electrochemical characteristics on a Ni patterned anode. In this paper, we use their experimental impedance spectra and polarization curve measurements for CO electrochemical oxidation on nickel/yttria-stabilized zirconia (Ni/YSZ) patterned anode, and examine possible limiting steps in CO oxidation kinetics. We consider four possible reaction mechanisms for CO electrochemical oxidation at Ni/YSZ anode, as shown in Table 1. Mechanism I is taken from Etsell and Elengas [12], and involves gaseous species or species adsorbed on the surface of the electrode and/or the electrolyte. In mechanism II, the oxidation of adsorbed CO by O²⁻ in the electrolyte is proposed. Mechanism Is and IIs are constructed by adding the surface diffusion steps to Mechanism I and II, respectively. These kinetic mechanisms are illustrated in Fig. 1, in which the geometry is similar to that used in the experimental setup of the patterned Ni anode button cell on a YSZ single crystal with LSM/YSZ porous cathode investigated by Habibzadeh et al. [11].

Figure 1. Patterned Ni patterned anode geometry and elementary reaction pathways.

We propose an 1D comprehensive electrochemical oxidation model for the prediction of the steady-state polarization curve of a patterned anode SOFC. The model utilizes one of the CO electrochemical oxidation mechanism described in Table 1 and incorporates either of the two charge transfer steps shown in Table 1, that is: the O charge transfer or the CO charge transfer, as well as surface diffusion processes. Some of the model parameters are given and others are adjusted to match experimental polarization curves. We use the experimental data to determine the electrochemical mechanism most likely to predict the measurements accurately.
Table 1 CO electrochemical oxidation mechanisms

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Reaction</th>
<th>Δϕ (cm, mol, s)</th>
<th>n°</th>
<th>E° (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>CO adsorption CO(g)+(Ni) ⇌ CO(Ni)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O charge transfer</td>
<td>O²⁻(YSZ)+(Ni) ⇌ O(Ni)+(YSZ)+2e⁻</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>adsorbed CO reaction</td>
<td>CO(Ni)+O(Ni) ⇌ CO₂(Ni)+(Ni)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂ desorption</td>
<td>CO₂(Ni) ⇌ CO₂(g)+(Ni)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Is</td>
<td>Mechanism I with adsorbed species surface diffusion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>CO adsorption CO(g)+(Ni) ⇌ CO(Ni)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO charge transfer</td>
<td>CO(Ni)+O²⁻(YSZ) ⇌ CO₂(Ni)+(YSZ)+2e⁻</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂ desorption</td>
<td>CO₂(Ni) ⇌ CO₂(g)+(Ni)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IIa</td>
<td>Mechanism II with adsorbed species surface diffusion</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The model equations and parameters are described in detail in Section 2. The results are obtained and discussed in Section 3. Finally conclusions are stated in Section 3.

2. Model development

Model geometry and assumptions

The model assumptions are:
(1) Gases are modeled as ideal gases.
(2) The temperature of the cell is uniform. All parameters are evaluated at the given temperature.
(3) The electrochemical mechanism is modeled using a set of elementary reactions that represent chemical reactivity at the molecular scale. Heterogeneous thermochemical and electrochemical reactions are assumed to take place on both of the Ni surface and YSZ surface.
(4) The charge transfer reaction is assumed to be a surface spillover reaction taking place at the TPB as shown in Fig. 1. Two different reaction pathways are studied.
(5) Surface diffusion is one-dimensional and is modeled as Fickian diffusion along the surface in the direction perpendicular to the B.
(6) One adsorbed CO molecule occupies one vacant position on the surface, neglecting the possibility of two vacant positions being occupied by a single CO molecule.

(7) The microstructure of the cathode is stable and homogeneous. The distributions of the two conducting phases (electronic and ionic) in the electrodes are assumed to be uniform.

In order to simplify the calculation, the three-dimensional domain shown in Fig. 1 is mapped onto a one-dimensional computational domain as shown in Fig. 2. In this figure, the model structures, calculation domains and boundaries are labeled schematically, as described later.

Figure 2. Representation of the 3D cell using a 1D calculation domain

Using the above assumptions and the simplified model geometry, a 1D SOFC model is formulated considering anodic heterogeneous chemistry, electrochemistry, charge and mass balance, as described in the following sections.

Governing equations

A. Anode heterogeneous chemistry

Heterogeneous chemistry at the catalytic surface of the anode is used. Ni is an effective catalyst for surface reactions, especially for hydrocarbon fueled SOFC. A simplified heterogeneous mechanism from Hecht et al. 13, Janardhanan et al. 14 and Zhu et al. 15 is used, as shown in Table 2.

Table 2 Heterogeneous reactions mechanism on the Ni surface

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Δϕ (cm, mol, s)</th>
<th>n°</th>
<th>E° (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>O₂ + Ni(s) + Ni(s) → O(s) + O(s)</td>
<td>1.000×10⁻² b</td>
<td>0</td>
</tr>
<tr>
<td>1f</td>
<td>CO₂ + Ni(s) → CO₂(s)</td>
<td>1.000×10⁻⁵ b</td>
<td>0</td>
</tr>
<tr>
<td>2f</td>
<td>CO + Ni(s) → CO(s)</td>
<td>5.000×10⁻¹ b</td>
<td>0</td>
</tr>
<tr>
<td>3f</td>
<td>Desorption</td>
<td>O(s) + O(s) → Ni(s) + Ni(s) + O₂</td>
<td>4.283×10⁻²³</td>
</tr>
<tr>
<td>1b</td>
<td>CO₂(s) → CO₂ + Ni(s)</td>
<td>6.447×10⁻⁷</td>
<td>0</td>
</tr>
<tr>
<td>2b</td>
<td>CO(s) → CO + Ni(s)</td>
<td>3.563×10⁻¹¹</td>
<td>0</td>
</tr>
<tr>
<td>3b</td>
<td>θ(CO₂)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface reactions</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The sticking coefficient $S_i^0$ is temperature dependent and is expressed as

$$S_i^0 = a_i T^b \exp \left( -\frac{d_i}{RT} \right)$$

where $a_i$ and $b_i$ are dimensionless parameters and $d_i$ has units of $RT$. The parameters are listed in Table 1.

For the YSZ surface, few validated reaction mechanisms are available in the literature. Vogler et al.\textsuperscript{10} considered molecular adsorption and desorption of water, water dissociation, and bulk-surface exchange. In this study, we neglect CO and CO\textsubscript{2} adsorption and desorption on the YSZ surface, and only consider the bulk-surface exchange of oxygen. Transport of bulk oxygen species takes place by a vacancy diffusion mechanism. The reaction formula and reaction data is given by

$$\text{O}_2^- (\text{YSZ}) + \text{O} (\text{YSZ}) \rightleftharpoons \text{O}_2^- (\text{YSZ}) + \text{O} (\text{YSZ})$$

where, $k_{\text{YSZ},1b}$ is determined from mass action kinetics, $k_i = k_{i0} \exp \left( -\frac{E_i}{RT} \right)$ with $k_{i0} = 1.6e22$ cm$^2$/mol s, and activation energy $E_i = 90.9$ kJ/mol. $k_{\text{YSZ},1b}$ is determined from the equilibrium constant.

\section*{Anode electrochemistry}

Two charge transfer pathways, corresponding to mechanism I and II in Table 1, are considered in this study:

$$\text{O}_2^- (\text{YSZ}) + \text{O} (\text{YSZ}) \rightleftharpoons \text{O}_2^- (\text{YSZ}) + \text{O} (\text{YSZ})$$

where, $k_{\text{YSZ},2b}$ is determined from mass action kinetics, $k_i = k_{i0} \exp \left( -\frac{E_i}{RT} \right)$ with $k_{i0} = 1.6e22$ cm$^2$/mol s, and activation energy $E_i = 90.9$ kJ/mol. $k_{\text{YSZ},2b}$ is determined from the equilibrium constant.
The Velec, an is the electronic potential of nickel at the TPB interface and defined as follows:

\[ \eta_{\text{an}} = V_{\text{elec,an}} - V_{\text{ref,an}} \]  

(14)

In this study, the anode reference potential \( V_{\text{ref,an}} \) was set to zero. The \( V_{\text{elec,an}} \) is the electronic potential of nickel at the TPB interface and \( V_{\text{ion,an}} \) is the ionic potential at the TPB interface.

The parameters \( k_{\text{an},\text{f,CO}}^0, k_{\text{an},\text{f,CO}}^0, k_{\text{an},\text{i,O}}^0, k_{\text{an},\text{i,O}}^0 \) are calculated from:

\[ k_{\text{an},\text{f,CO}}^0 = \frac{i_{\text{h,CO}}}{2F\eta_{\text{CO}}^0} \]  

(15)

\[ k_{\text{an},\text{i,O}}^0 = \frac{i_{\text{h,O}}}{2F\eta_{\text{O}}^0} \]  

(16)

where \( i_{\text{h}} \) is the exchange current density, \( c^i \) denotes the species surface concentrations at equilibrium.

The exchange current density are written in the following form:

\[ i_{\text{h,CO}} = k_{\text{h,CO}} \exp \left( -\frac{\Delta G_{\text{CO}}}{RT} \right) \]  

(17)

where \( k \) and \( \Delta G \) are treated as tuning parameters when comparing the simulated polarization curve with the experimental results.

C. Charge balance

For the anode, the charge balance equations considering the transient effects of the double-layer capacitance are formulated as follows:

\[ i_t = i_{\text{h,CO}} + \frac{\partial (C_{\text{elec}} \Delta V_{\text{TPB}})}{\partial t} \]  

(18)

where \( t \) is time, \( C_{\text{elec}} \) is the specific interface double-layer capacitance between Ni and YSZ.

The cathode ionic charge and electronic charge equations are:

\[ \frac{\partial (C_{\text{elec}} S_{\text{TPB,el}} (V_{\text{elec,TPB}} - V_{\text{elec,TPB}}))}{\partial t} + \nabla \cdot (-\sigma_{\text{elec}}^0 \nabla V_{\text{elec,TPB}}) = Q_{\text{elec,TPB}} \]  

(19)

\[ \frac{\partial (C_{\text{elec}} S_{\text{TPB,el}} (V_{\text{elec,TPB}} - V_{\text{elec,TPB}}))}{\partial t} + \nabla \cdot (-\sigma_{\text{elec}} \nabla V_{\text{elec,TPB}}) = 0 \]  

(20)

where \( V_{\text{elec}} \) and \( V_{\text{elec,TPB}} \) are the electronic and ionic electric potential, respectively. \( \sigma_{\text{elec}} \) is the corresponding conductor phase effective conductivity. \( C_{\text{TPB}} \) and \( C_{\text{bulk}} \) are the cathode oxygen concentrations at the TPB and in the bulk, respectively, \( \alpha \) is the charge transfer coefficient, \( n_x \) is the number of electrons participating in the reaction, and \( \eta_{\text{an}} \) is the cathode local overpotential, which is defined as [19]

\[ \eta_{\text{an}} = V_{\text{elec,an}} - V_{\text{ion,an}} - V_{\text{ref,an}} \]  

(21)

where \( V_{\text{ref,an}} \) is the cathode local relative potential difference between the electronic conductors at a reference state. The cathode reference potential \( V_{\text{ref,an}} \) equals to the actual cell open circuit voltage (OCV). Essentially, the SOFC is a concentration cell of O2 and the OCV are determined by Nernst equation:

\[ V_{\text{OCV}} = \frac{RT}{n_F} \ln \left( \frac{p_{\text{0}}^{\text{O}_2}}{p_{\text{0}}^{\text{O}_2}} \right) \]  

(22)

where \( p_{\text{0}}^{\text{O}_2} \) and \( p_{\text{0}}^{\text{O}_2} \) are the equilibrium oxygen partial pressures in the cathode and the anode, respectively. \( p_{\text{0}}^{\text{O}_2} \) can be determined by the heterogeneous reactions and the compositions of fuel in the anode.

Heterogeneous reactions rates and electrochemical reactions rates depend on the concentration of surface species. In order to obtain the reaction rates at the anode, the effective reaction rates for all reactions per unit volume is needed. According to the model assumptions, the heterogeneous reactions and electrochemical reactions only take place at the Ni surface and TPB, respectively. Therefore, the Ni active surface area per unit volume, \( S_{\text{Ni}} \), and the TPB active area per unit volume, \( S_{\text{TPB}} \), in the anode should be specified.

The area \( S_{\text{TPB}} \) is formulated using the particle coordination number in binary random packing of spheres using the percolation theory [19, 20]

\[ S_{\text{TPB}} = \pi \sin^2 \theta \sin \theta \frac{n_{\text{el}} n_{\text{el}}}{Z_{\text{el}} Z_{\text{el}}} P_{\text{el}} P_{\text{el}} / Z \]  

(23)

where \( Z \) is the mean coordination number, \( r_{\text{el}} \) is the mean radius of the electronic conductor particle, \( \theta \) is the contact angle between the electronic and ionic conductors particles, \( n_{\text{el}} \) is the total number of particles per unit volume, \( n_{\text{el}} \) and \( n_{\text{io}} \) are the fraction number of electronic and ionic conducting particles, \( Z_{\text{el}} \) and \( Z_{\text{io}} \) are the coordination numbers of the electron and the ion conducting particles, and \( P_{\text{el}} \) and \( P_{\text{io}} \) are the whole range connection probabilities of the same particles.

The cathode exchange current density \( i_{\text{h,el}} \) is expressed as:

\[ i_{\text{h,el}} = \frac{\beta RT}{4F} \exp \left( \frac{E_a}{RT} \right) \left( \frac{p_{\text{0}}^{\text{O}_2}}{p_{\text{0}}^{\text{O}_2}} \right)^{0.25} \]  

(24)

where \( E_a \) is 130,000 J mol\(^{-1}\), and \( \beta \) is 5.76e10\(^{31}\).

There are no double-layer capacitance effects or current sources or sinks in the electrolyte. Thus, the electrolyte charge balance equation is reduced to

\[ \nabla \cdot (-\sigma_{\text{elec}} \nabla V_{\text{elec,el}}) = 0 \]  

(25)

where \( \sigma_{\text{elec}} \) is the effective ionic conductivity of electrolyte and \( V_{\text{elec,el}} \) is the potential in the electrolyte.

D. Mass balance

For the anode, the species production rates follow mass-action kinetics, and the species transport on the Ni and YSZ surfaces can be described in the following form:

\[ \frac{\partial q}{\partial t} = \sigma_{\text{eff}} \nabla \cdot \left( D_{\text{surf}} \nabla \left( \Gamma \theta \right) \right) \]  

(26)

where, \( D_{\text{surf}} \) denotes the surface diffusion coefficients. We have collected a compilation of surface diffusion coefficients from various
literature sources and tried to set the lowest value and highest values from literature as the estimation limits.

The extended Fick’s model (EFM) is used to describe the mass transfer in the porous cathode, and the effect of finite pressure gradient is neglected. The EFM equation is written as follows:22,

\[
e^\varepsilon \frac{\partial c_k}{\partial t} + V \left(-D_k^{\text{eff}} \nabla c_k\right) = R_k
\]

(27)

where \( \varepsilon \) is the porosity of the electrode, \( c_k \) is the gas molar concentration, \( R_k \) is the mass balance source term of the gaseous species inside the porous medium, and \( D_k^{\text{eff}} \) is the effective diffusivity of gaseous species \( k \). Molecular diffusion and Knudsen diffusion are dominant for large pore sizes and when the pore sizes are smaller than molecular mean-free path, respectively. The effective diffusivity \( D_k^{\text{eff}} \) is written as:

\[
D_k^{\text{eff}} = \left( \frac{1}{D_k^{\text{mole}}} + \frac{1}{D_k^{\text{Kn}}} \right)^{-1}
\]

(28)

where \( D_k^{\text{mole}} \) and \( D_k^{\text{Kn}} \) is the effective molecular diffusion coefficient and effective Knudsen diffusion coefficient, respectively.

### Table 1 Boundary conditions

<table>
<thead>
<tr>
<th>Boundary</th>
<th>Ionic charge</th>
<th>Electronic charge</th>
<th>Surface species mass balance</th>
<th>Gas mass balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/gas interface</td>
<td>—</td>
<td>( V_{\text{an}} )</td>
<td>Insulation</td>
<td>( c_{\text{CO},c_{\text{CO}_2}} )</td>
</tr>
<tr>
<td>TPB</td>
<td>( i_{\text{CO}} ) or ( i_{\text{O}} )</td>
<td>-( i_{\text{CO}} ) or -( i_{\text{O}} )</td>
<td>Molar flux</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CO(Ni): (-i_{\text{CO}}/2F)</td>
<td></td>
</tr>
<tr>
<td>Cathode/electrolyte interface</td>
<td>Continuity</td>
<td>Insulation</td>
<td>Insulation</td>
<td>( c_{\text{CO}<em>2}, c</em>{\text{N}<em>2}, c</em>{\text{N}_2} )</td>
</tr>
<tr>
<td>Cathode/gas interface</td>
<td>Insulation</td>
<td>( V_{\text{ca}} )</td>
<td>—</td>
<td></td>
</tr>
</tbody>
</table>

The boundary conditions “insulation” and “continuity” refer to a zero partial derivative and a continuous flux at the boundary, respectively. The difference between \( V_{\text{an}} \) and \( V_{\text{ca}} \) is the cell operating voltage.

### Solution method

Calculations were performed using the finite element commercial software COMSOL MULTIPHYSICS®, Version 3.2. The cell performance was calculated at a given cell voltage \( V_{\text{ca}} \). In order to compare with the experimental measurement, a linear scan of the voltage \( V_{\text{ca}} \) at rate of 10mV/s was used in the calculation, which was the same as that used to produce the experimental polarization curve. For the 1D SOFC model, the average current density at a given cell voltage was treated as that in the electrolyte.

### 3. Simulation and discussions

#### Model parameters

Table 3 lists the cell properties and some of the model parameters.
Concentration of oxygen vacancy in the YSZ (\(c_{\text{V}_\text{O}}\))

\[4.65 \times 10^3\ \text{mol m}^{-3}\]

The parameters \(\alpha, (i_{0,\text{CO}}, D_{\text{CO}(\text{Ni})})\) and \((i_{0,\text{O}}, D_{\text{O}(\text{Ni})})\) are tuned to produce the best fit with the experimental results.

Comparing Mechanisms I and II

A. Mechanism I - CO charge transfer based mechanism

There are three fitting parameters: the charge transfer coefficient, \(\alpha\), the exchange current density, \(i_{0,\text{CO}}\), and the surface diffusion coefficient, \(D_{\text{CO}(\text{Ni})}\). Coefficients in these parameters were varied until the model predictions give the best fit for the experimental results. These results are shown in Fig. 3. The resulting expressions for the fitting parameters are as follows.

\[
\alpha = 0.6 \quad \text{(30.a)}
\]

\[
i_{0,\text{CO}} = 1.68 \times 10^5 \exp \left(\frac{-165615}{RT}\right) \text{Am}^{-1} \quad \text{(30.b)}
\]

\[
D_{\text{CO}(\text{Ni})} = 2.85 \times 10^3 \exp \left(\frac{-160518}{RT}\right) \text{m}^2/\text{s} \quad \text{(30.c)}
\]

![Figure 3. Experimental polarization curves and simulated results using CO charge transfer mechanism](image)

Figure 3. Experimental polarization curves and simulated results using CO charge transfer mechanism

At 750°C, the surface diffusion coefficient of CO(Ni), calculated from Eq. (30.c), is around 1.82e-13 m²/s. According to the published data in literatures, the surface diffusion coefficient of adsorbed CO on Ni surface is in the range of 2.5e-6 to 4.95e-13 m²/s, depending on the surface properties, crystal type, surface coverage as well as measuring method. The value predicted from Eq. (30.c) is within the published range.

To further check the model validity using the CO charge transfer mechanism, the computed Tafel plots is compared with the experimental results, as shown in Fig. 4. The model results agree well with the experimental data.

B. Mechanism II - O charge transfer based mechanism

The three fitting parameters are as follows.

\[
\alpha = 0.6 \quad \text{(31.a)}
\]

\[
i_{0,\text{O}} = 1.68 \times 10^5 \exp \left(\frac{-165615}{RT}\right) \text{Am}^{-1} \quad \text{(31.b)}
\]

\[
D_{\text{O}(\text{Ni})} = 6 \times 10^3 \exp \left(\frac{-117400}{RT}\right) \text{m}^2/\text{s} \quad \text{(31.c)}
\]

The surface diffusion coefficients of O(Ni) species was directly taken from Vogler et al. While the CO charge transfer mechanism is able to reproduce the experimental polarization curves rather well, this is not the case when attempting to fit the polarization curves using a model considering the O charge transfer mechanism, as shown in Fig. 5. For instance, at 725°C, we kept all the parameters the same as in CO charge transfer mechanism model. We got the “base case” curves shown in Fig. 5(a). It can be seen that the simulated curve largely underestimate the experimental results. Next, a parametric analysis of O(Ni) surface diffusion coefficients was carried out. It was found that the deviation between the simulated and the experimental results could be reduced by increasing the O(Ni) surface diffusion coefficient. However, even when the value of O(Ni) surface diffusion coefficient was increased to (1e12) times the value used in base case, the simulated polarization curves still underestimated the experimental measurements. In addition, when O(Ni) surface diffusion coefficient was increased from (1e9) to (1e12) times the original value, the polarization curves hardly changed. Next, we increased the value of \(i_{0,\text{O}}\) to twice its base case value, as shown in Figure 5(b), and found that the curve moved close to the experimental curves. Although the model with the O charge transfer mechanism could now predict the experimental results better, the value of model parameters, e.g. O(Ni) surface diffusion coefficient, is not reasonable. Therefore, we concluded that the CO charge transfer mechanism could better predict the cell performance while using more physically
reasonable parameters.

Figure 5. Experimental polarization curves and simulated results using the O charge transfer mechanism (a) Parametric analysis of O(Ni) surface diffusion coefficient (b) Parametric analysis of exchange current density of the O charge transfer reaction

**Species surface concentration**

Spatial profiles of the surface concentration of CO(Ni) and O(Ni) species at 200 mV are shown in Fig. 8 at 725 °C and 775°C and different polarization voltage (200, 400mV), obtained using the CO charge transfer mechanism model. Simulated results show strong concentration gradients within 3e-7 m of the TPB and at different operating conditions.

Figure 8. CO(Ni) surface concentration distribution near TPB

The results show that the surface concentration of CO(Ni) at 725 °C, which is mainly determined by the adsorption/desorption equilibrium, is higher than that at 775 °C. On the other hand, it can be seen that the surface gradient is larger at lower temperature and higher polarization voltage. At lower temperature, the surface diffusion is slower and the CO(Ni) surface concentration gradient is larger. At higher polarization voltage, the consumption rate of CO(Ni) at the TPB interface is faster, which also leads to larger CO(s) surface concentration gradient. This agrees well with the quantitative conclusion from the experimental EIS spectra analysis by Matsuzaki et al., and suggests that at lower temperature and higher polarization voltage, the surface diffusion may be an important limiting step.

4. Conclusion

A 1D comprehensive electrochemical oxidation model is proposed for the prediction of the steady-state polarization curve of a patterned anode SOFC. The model incorporates either of the two charge transfer steps: O charge transfer and a CO charge transfer, and surface diffusion processes. The model is used for the quantitative investigation of the cell performance as well as microscopic elementary reactions and diffusion steps. The model is also used to predict the concentration distribution of surface species near the three-phase boundary (TPB). The main conclusions of the paper are:

1. Both of the models with O charge transfer and CO charge transfer mechanism are able to predict the experimental polarization curves. However, the model with CO charge transfer mechanism predicts the cell performance more accurately while incorporating physically reasonable values for the surface diffusion coefficient.
2. The surface concentration gradient is larger at lower temperatures and higher polarization voltages. Thus, surface diffusion may be one of the important limiting steps at lower temperature and higher polarization voltage.

References


