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Mass-Action Kinetics Approach to Concurrent H₂ and CO Electrochemistry in a Patterned SOFC Anode

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SOFC is a fuel flexible technology suitable for producing clean energy. Understanding of the multi-reaction mechanism that a complex H₂-CO fuel presents to the electrochemical kinetics is numerically approached in this work. By using existing fundamental reaction mechanisms and kinetic parameters, elementary reactions involved in an SOFC anode have been assembled, modeled and analyzed. This involves both homogeneous and heterogeneous chemistry, electrochemistry and surface diffusion. The use of the patterned anode approach removes the mass transport complications and allows comparison with pre-existing experimental data. The model provides both polarization curves and surface coverage distribution, among other results, providing a high level of detail and understanding of the physical phenomena involved. In particular, analysis is focused upon understanding how the competitive H₂ and CO reactions behave. The presence of CO was found to stabilize OCV response to temperature and while it occupied most of the active sites it did not penalize overall performance except when significant product species were present.

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The operation of SOFC with both gaseous¹⁻⁴ and even liquid hydrocarbons⁵ has been widely discussed, analyzed, and reported in the literature taking both experimental and analytic approaches.

Particular attention has been put in fuel cell and reformer integration. By analyzing several degrees of internal and external reforming, it has been pointed out by Margalef et al. that the use of Direct Internal Reforming (DIR) in High Temperature Fuel Cells (HTFC) presents an efficiency advantage.⁶ Because of the presence of carbon in hydrocarbon molecules, analysis of carbon deposition and coking, a key issue for fuel cell durability and, ultimately, its commercialization, has been and discussed by Klein et al.³

Following Mizusaki's pioneering work,⁷ assuming that H₂ is the only electro-active species in a H₂-CO mixture is common in the literature.^{3,8,9} However, Sureshini et al. results suggest that CO can be incorporated to the fuel stream and provide similar performance to that of pure H₂, even at H₂ concentrations as low as 25%.¹⁰

These results open a new research paradigm, as interest in concurrent electrochemical reactions is renewed. For doing so, an elementary approach to the system of equations is required. Unfortunately, the elementary electrochemical mechanisms and kinetic constants are still among the less understood phenomena of the fuel cell community.¹¹ For this reason, researchers have been widely using a simplified approach, the Butler-Volmer equation.

The Butler-Volmer equation has the advantage of simple solution, but, it presents several disadvantages when simulating a competitive reacting scenario. Even though this approach has been used previously for concurrent reactions,¹² it presents several drawbacks, as it assumes that *a*) charge-transfer occurs in a single step, *b*) composition is at equilibrium, *c*) there is a known current exchange density, which most of the times is a value that needs to be fitted; finally, and most importantly *d*) it does not account for the competition of active sites that multiple reaction systems will present.

These disadvantages can be addressed by taking a fundamental approach to the competing rates of elementary electrochemical reactions. Surface diffusion has to be taken into account as well. This approach requires the characterization of all the kinetic parameters of all chemical and electrochemical steps involved in the mechanism. This approach was first stated by Bessler et al.^{13,14} and has gained popularity in recent years.

Hecht et al.¹⁵ and Janardhanan and Deutschmann¹⁶ proposed a detailed mechanism for the reforming of methane in an SOFC anode and its kinetic characterization, including homogeneous and heterogeneous chemistry.

By fitting the electrochemical parameters to the experimental results, new mechanisms for H₂ and CO electrochemistry have been

proposed, characterized and discussed. Other authors, such as Moyer et al.¹⁷ have applied this approach for modeling conventional tubular solid oxide cells.

In order to reduce the uncertainty arising from the porous media characterization, a simplified geometry is commonly used in these analysis. Most importantly, TPB density should be known and perfectly determined. This approach has been used in experiments performed by Mizusaki et al.,^{18,19} Sureshini et al.¹⁰ and Habibzadeh et al.,^{20,21} among others.

The modeling of these experiments has been successfully implemented by Goodwin et al.,²² Yurkiv et al.^{23,24} and Hanna et al.,²⁵ among others.

Although there is still some debate among the scientific community about the chemical and electrochemical details of the mechanisms involved, it seems clear that single channel hydrogen spillover is the rate-controlling reaction for H₂, as stated by Vogler et al. in Ref. 27, while the reaction mechanism for CO electrochemistry is still unclear.¹¹

Model Formulation

Domain.—Figure 1 presents a drawing of a patterned anode cell. Ni strips act as the anode. Ni provides good catalytic activity and is a common material used in commercial fuel cells. The width of the strips depends upon the experimental setup, but normally it is between 50 and 100 μm . The spacing between them is normally the same as the width. As a reference, Mizusaki et al. experiments were performed with an 8 mm diameter, 1 mm thick YSZ substrate over which 0.5–1 μm thick Ni strips were deposited. More details can be found in Ref. 7.

A conventional yttria-stabilized zirconia (YSZ) pellet acts as the electrolyte. YSZ is assumed to be homogeneous and mono-crystalline, and so the flux of ions flowing to the anode strips is considered homogeneous.²²

Anode active area is the contact line between the Ni strip and the YSZ pellet. It is well-defined and known.

The cathode is formed by Pt paste that is screen printed on the YSZ pellet. Because of the exceptional catalytic activity of Pt and the huge amount of active sites that a porous structure provides compared to the patterned one (i.e., the anode side) thermodynamic equilibrium is assumed at the cathode. This approach is supported by the experimental work performed by Mizusaki et al.⁷

Note that the porosity of the cathode provides way more active sites than the patterned anode. For this reason, the current density is different at both electrodes.

The cell is enclosed in a furnace to control its temperature. Due to the small geometry of the cell and the large thermal mass of the

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Figure 1. Electrolyte-supported patterned anode cell. Ni strips are used as anode, while Pt paste is used for the cathode. Electrolyte is made of YSZ.

furnace, temperature gradients in the cell are neglected and so the case is considered isothermal.

Gas concentrations on both chambers are controlled. Because of the low current density at which the experimental setup is operating, gas concentrations are assumed to be constant and known.

Under the assumptions listed above, the phenomena are just functions of the distance from the active area and time. Consequently, it is possible to map them into a 1D region.²² Figure 2 illustrates this assumption.

Potentials and current.—All surfaces present in the cell are assumed to be equipotential surfaces. Due to the high conductivity of both electrodes and the low current densities occurring in a setup like this, both electronic and ionic ohmic losses at the electrodes and the electrolyte are neglected.²² In this effort the assumption of negligible ohmic potential drop across the electrodes and electrolyte, which hinges upon low current density operation, are exactly the same as those used by Goodwin et al.²²

The potentials of the electrodes are the same for the surface and the bulk. Figure 3 shows all the potentials involved in the cell and the corresponding overpotentials in which we are interested. Note that the TPB is just at the junction of the electrolyte and the corresponding electrode.

Anode and cathode overpotentials drive the electrochemical reactions taking place through the corresponding TPBs. They arise from the difference in electrochemical potentials of the surfaces. On the other hand, the ohmic loss is due to a simpler mechanism: the flux of ions through the electrolyte produces a potential drop which lowers the voltage.

The voltage that the cell provides is calculated as: $E_{cell} = \Phi_a - \Phi_c$. This can be calculated as well by $E_{cell} = \Delta V_a + \Delta V_{\Omega} + \Delta V_c$.

Figure 2. Map of electrode-electrolyte into a 1D domain.

Figure 3. Cell potentials. Φ_a is the potential at the anode, Φ_a^e is the potential of the electrolyte surface at the anode side, Φ_c^e is the potential of the electrolyte surface at the cathode side, and Φ_c is the potential at the cathode. The voltage differences are ΔV_a , the anode overpotential, ΔV_{Ω} , the ohmic loss, and ΔV_c , the cathode overpotential.

Because of the low cathode current density, and the good catalytic activity of Pt, cathode reactions are considered to be in equilibrium. In this way ΔV_c is constant and known. Further details regarding the calculation of ΔV_c will be provided in Equilibrium section.

Due to the low current density at which the experimental setup operates and the excellent electrical conductivity of both electrodes, electronic ohmic losses are neglected.^{19,22}

The use of current density j (normally in mA/cm^2 and its multiple A/m^2) is common in most of the electrochemical literature. This is a convenient measure correlating current production with superficial measurable area rather than a physically derived quantity when talking about current production, since active sites are unidimensional domains (lines) with the natural measurement unit of m . Most of the times, as this quantification is extremely complicated in a porous media, active area is given as the measurable dimension of the cell. However, in the patterned electrode case, as the anode presents well-defined active sites at the nickel-YSZ interface, the working quantity is the total amount of current per active site, that is, mA/m and its multiple A/m . Note that the regular units mA/cm^2 and its multiple A/m^2 are only preferred when considering a porous and complex 3-dimensional anode electrolyte interface.

O^{2-} ions moving from the cathode to the anode require a potential gradient to move through the electrolyte. This will result in electrolytic ohmic losses. According to Ohm's law²²

$$\Delta V_{\Omega} = i \frac{t_{\text{electrolyte}}}{\sigma_{\text{electrolyte}}} \quad [1]$$

where i is the current density of the cell in A/m^2 , t is the thickness of the electrolyte in m , and σ is the ionic conductivity in S/m . However, again, due to the low current density at which the setup operates, and the fact that such a loss does not materially affect the electrochemical kinetic phenomena of interest, this loss is assumed to be negligible.^{19,22}

The anode-electrolyte interface does not allow charge carriers to cross from one side to the other (i.e., ions cannot move into the electrode nor electrons in the electrolyte) and thus the build-up of charge at the interface presents an effective capacitance, or charge double layer. The transient charge balance is given by²²

$$\frac{dq_{dl}}{dt} + i_F = i_{total} \quad [2]$$

where q_{dl} is the balance of charge at the double layer in C , i_F is the current due to the electrochemical reactions only in A, and i_{total} is the total current provided coming from the external circuit in A.

Where the charge balance is given by the superposition of the Faradic reactions plus the transient charge flow due to the double

layer capacitance. Note that in a capacitor¹³

$$\frac{dq_{dl}}{dt} = A_{dl} C_{dl} \frac{\partial V}{\partial t} \quad [3]$$

where A_{dl} is the area of the double layer region in m^2 , C_{dl} is the capacitance of the double layer in F , and V is the voltage difference at which the double layer is subjected in V .

However, the effect of the double layer charge or discharge is only important when modeling the transient response of the system (e.g., under EIS). Because only steady state is studied in this model, $\frac{dq_{dl}}{dt} = 0$.

Transport.—The set of equations that govern surface coverage are described by the reaction-diffusion equation as follows²²:

$$\frac{\partial [X_i]}{\partial t} - D_i \frac{\partial^2 [X_i]}{\partial x^2} = \dot{S}_i \quad [4]$$

where X_i is the concentration of species i in $kmol/m^2$, D_i is the diffusivity of species i in m^2/s and $\dot{S}_i$ is the source/sink term of species i in $kmol/m^2/s$.

Vacancy sites are considered as an extra species in this equation.²⁶ This accounts for the availability and the mobility of active sites along the surface as well.

Low coverage has been assumed for the diffusion of species. Following Vogler and co-workers,²⁷ a surface-adapted Fickian approach to surface diffusion is used. It implies that species diffusivity is expressed by a temperature-activated equation only as follows:

$$D_i = D_i^0 \exp\left(\frac{-E_i^d}{RT}\right) \quad [5]$$

where D_i^0 is the pre-exponential factor in m^2/s , E_i^d is the activation energy in kJ/mol , R is the universal constant of gases in $kJ/mol/K$ and T is the temperature in K .

Nonetheless, it is known that species concentrations themselves may influence the mobility of ions. Unfortunately, there is a lack of correlations in this field. However, considering the good results that others have previously obtained using this approach^{22–25,27} we have elected to use 5 in this work as well. An extended work in this field can be found in Mogensen and Skaarup.²⁸

Equation 4 can be expressed in terms of surface coverages by¹³

$$\frac{\partial \theta_i}{\partial t} - D_i \frac{\partial^2 \theta_i}{\partial x^2} = \frac{\dot{S}_i}{\Gamma_s} \quad [6]$$

where θ_i is the surface coverage of species i , Γ_s is the concentration of active sites in surface s in $kmol/m^2$.

Remember that, by definition²⁶

$$\theta_i = \frac{[X_i]}{\Gamma_s} \quad [7]$$

In addition, if the number of active sites is conserved (i.e., $\Gamma = ct.$), as it is assumed in this case²⁶

$$\sum_{i=1}^N \theta_i = 1 \quad [8]$$

where N is the total number of species.

The repetitive domain imposes the symmetry boundary conditions²² at the ends of both the electrode

$$\left. \frac{\partial [X_i]}{\partial x} \right|_{x=L_{electrode}} = 0 \quad [9]$$

and the electrolyte.

$$\left. \frac{\partial [X_i]}{\partial x} \right|_{x=L_{electrolyte}} = 0 \quad [10]$$

For the TPB, considered as the junction between two different domains (i.e. electrode and electrolyte) the boundary condition is that

the contributions depend upon the electrochemical reactions only.²²

$$D_i \left. \frac{\partial [X_i]}{\partial x} \right|_{x=0} = \dot{S}_i^{TPB} \quad [11]$$

Chemistry.—*Thermal kinetics.*—Adsorption and desorption of species in both the electrode and the electrolyte surfaces, coupled with surface diffusion, are the mechanisms through which the TPB receives reactants and releases products to and from the gas. Fortunately, most of the reactions over Ni and YSZ involved in our case are well known and described, as done by Hecht et al. and Janardhanan and Deutschmann in their celebrated mechanism for the reformation of methane (CH_4) over a Ni-YSZ system.^{8,15,16} The basics of heterogeneous chemistry are well known and can be found in Ref. 26

Electrochemical kinetics.—Electrochemical reactions play a role in Equation 11, closing the system of equations at the TPB. Note that it is the only way that one surface can affect the other, as all the surface reactions involve only themselves and the gas phase.

A general electrochemical reaction can be written as^{13,22}

where R is the total number of reactants, P is the total number of products, ν_i is the stoichiometric coefficient for species i and M_i is the corresponding species. Note that this includes the presence of one electron. This is due to the fact that fundamental electrochemical reactions transfer a single electron at a time.

Forward and backward rates of the reaction are defined as^{13,22,26}

$$q_f = k_f \prod_{r=1}^R c_r \quad [13]$$

and

$$q_b = k_b \prod_{p=1}^P c_p \quad [14]$$

where q is the rate of reaction for each corresponding direction in $kmol/s$. k is the reaction constant for corresponding direction in $1/kmol^N/m^D/s$, where N is the number of species involved (i.e.,

R or P) and D is calculated as $D = \sum_{i=1}^N d_i$, where d_i is the dimension

of the phase where the species i is located. This is done in order to keep unit consistency when different phases, with eventually different dimensions, are involved. With this, the rate of reaction units are forced to be $kmol/s$. c_i is the concentration of species i in $kmol/m^d$.

The calculation of the reaction constants are conducted adding an extra term to the regular Arrhenius form used for heterogeneous chemistry. This takes into account the electric potential driving the reactions.^{13,22}

$$k_f = A_f \exp\left(\frac{-E_a^f}{RT}\right) \exp\left(\beta_a \frac{zF}{RT} \Delta\Phi\right) \quad [15]$$

and

$$k_b = A_b \exp\left(\frac{\Delta G}{RT}\right) \exp\left(\beta_c \frac{zF}{RT} \Delta\Phi\right) \quad [16]$$

where A is the pre-exponential coefficient of the Arrhenius formula in $1/kmol^N/m^D/s$, E_a is the activation energy in kJ/mol , R is the gas constant in $kJ/mol/K$, T is the temperature in K , β is the symmetry factor in the anodic or cathodic direction, z is the number of electrons involved in the reaction (for elementary reactions $z = 1$), F is Faraday's constant in $C/kmol$ and $\Delta\Phi$ is the potential difference between the different phases involved in the reaction in V (i.e., ΔV_a or ΔV_c , as shown in Figure 3).

In order to keep these relations thermodynamically consistent, microscopic reversibility has to be satisfied.¹⁴ This is imposed by

forcing the ratio of kinetic rates to be equal to the thermodynamic equilibrium constant²² according to

$$K_{eq} = \frac{k_f}{k_b} = \exp\left(\frac{-\Delta G^\circ}{RT}\right) \quad [17]$$

where: K_{eq} is the equilibrium constant for those conditions. It is non-dimensional. ΔG° is the change of free energy of the reaction in kJ/mol .

Note that microscopic reversibility is assumed in Equation 16,²⁷ and so only the characterization of one rate (normally the forward one) is required in order to determine the kinetics of the system, as the other one can be inferred from the thermodynamic data.¹³

$$k_b = k_f \exp\left(\frac{\Delta G^\circ}{RT}\right) \quad [18]$$

This is crucial as it requires the use of thermodynamically consistent data throughout all the mechanism. Otherwise, the prediction of the equilibrium potential will fail.¹⁴

Once the kinetics of the reactions have been determined, then the source terms of each species can be calculated by balancing the stoichiometry of the reaction according to^{13,22}

$$\dot{S}_i = \sum_{k=1}^{N_{\text{reactions}}} \nu_i^k (q_f - q_b) \quad [19]$$

For single electron transfer reactions $\beta_a + \beta_c = 1$, as β balances the effect of the potential difference in both anodic and cathodic directions. Often this value is assumed to be 0.5, even though it does not have to be necessarily the case.

Electrons have a particular treatment in the system. As they are released directly into the electrode, they are converted directly into current by means of

$$i_F = F \dot{S}_{e^-}^{TPB} l_{TPB} \quad [20]$$

l_{TPB} is the length of the TPB in m . alternatively, one can work with current density by recalling that $j_F = i_F / l_{TPB}$.

Equilibrium.—If the set of reactions is in equilibrium, an overall reaction can be extracted and its net potential can be calculated as^{22,29}

$$\Delta V = -\frac{\Delta G}{zF} \quad [21]$$

where z is the number of electrons involved in the reaction in kmol and

$$\Delta G = \sum_{p=0}^P \mu_p - \sum_{r=0}^R \mu_r \quad [22]$$

where μ_i is the electrochemical potential of the species i .

This is used to calculate the voltage contribution at the cathode side.

Note that ΔG can be stated as follows:

$$\Delta G = \Delta G_0 + kT \ln \frac{\prod_p a_p^{\nu_p}}{\prod_r a_r^{\nu_r}} \quad [23]$$

where ΔG_0 is ΔG at the reference state and a_i are product/reactant activities.

By substituting Equation 23 into Equation 21, and after rearranging terms, we obtain:

$$E = E_0 + \frac{RT}{zF} \ln \frac{\prod_p a_p^{\nu_p}}{\prod_r a_r^{\nu_r}} \quad [24]$$

where E_0 is the standard cell voltage. This is the well-known Nernst equation.

Model Implementation

The equations described in sections Potentials and current - Chemistry close the boundary conditions of the transport Equation 4.²² By solving the resulting system of equations, the species distribution over both the electrode and the anode surfaces can be resolved. In addition, a relation between current and voltage described through Equations 15 and 16 details the polarization characteristics of the system.

The number of unknowns in the system is $N + 2$, corresponding to N surface species plus the current and the voltage delivered by the cell. However, we can only impose N Equations for 4 plus Equation 20. For this reason, either i_F or ΔV has to be fixed in order to determine the other dependent variable. Most of the time, it is more convenient to use ΔV as the independent variable and then produce a polarization curve by computing the corresponding steady-state current output.

The system has been approached numerically by means of a Finite Volume Method that has been implemented in C++. A logarithmic spacing has been applied to both the electrode and the electrolyte surfaces with smaller spacing near the TPB region. The kinetics and local species concentration of the system have been resolved thanks to the C++ library CANTERA³⁰ which solved a pseudo-transient problem for every ΔV value of the polarization curve. Initial values of surface coverages were taken from the previous ΔV steady-state solution and evolved until the new steady-state solution was reached. The first iteration considered 50% Zr sites and 50% (χ) sites over YSZ and 100% of (Ni) sites over Ni strips.

H₂ mechanism.—The mechanism proposed by Goodwin et al.²² is used to obtain transport and chemical reactions rate parameters.

Surface Diffusion.—Diffusion is modeled as an activated process as it was described in Transport section. This requires the computation of the diffusion coefficient according to Equation 5. Table I presents the parameters used for computation of the diffusion coefficient as presented in Ref. 19.

Chemistry.—The hydrogen spillover mechanism proposed by Goodwin et al.²² is used.

Reactions over YSZ present the particularity of having two types of active sites: Zr and χ , where Zr represents a free zirconium atom and χ represents an oxygen vacancy.

The YSZ bulk contains oxygen ions (O^{2-}) and vacancies (V_O), which are balanced.

Electrochemical reactions occur at the TPB. They represent the most fundamental electrochemical principle behind the operating nature of a fuel cell and are the point of some disagreement among researchers in the scientific community. As commented previously, the mechanism chosen in this work is based upon the good results that Goodwin and co-workers presented.²² In their work, different mechanisms were explored and fitted to Mizusaki's experiments.¹⁹ Unfortunately, Mizusaki's experiments were performed at a single temperature of 700°C, and consequently no temperature dependency

Table I. Parameters for the calculation of D_i .²² On YSZ, diffusion coefficient over different active sites (i.e. Zr or χ) is substrate-independent.

species	D_i° [m^2/s]	E_i^d [kJ/mol]
Ni		
(Ni)	1.4×10^{-6}	93.20
H(Ni)	2.5×10^{-7}	14.65
H ₂ O(Ni)	1.4×10^{-6}	93.20
OH(Ni)	1.4×10^{-6}	93.20
O(Ni)	1.4×10^{-6}	93.20
YSZ		
H(YSZ)	5.0×10^{-12}	0.0
O(YSZ)	5.85×10^{-15}	49.0
OH(YSZ)	5.0×10^{-12}	0.0

Table II. Reaction mechanism for H₂.²² Active site density for Ni is $\Gamma = 1.7 \times 10^{-8} \text{ kmol/m}^2$ and for YSZ is $\Gamma = 2.5 \times 10^{-8} \text{ kmol/m}^2$. Because YSZ contains Zr and χ sites, they are split evenly.²²

	Reaction		A_f or γ_0 [mol, cm, s]	E^f or β [kJ/mol]
Ni	$\text{H}_2(\text{g}) + 2(\text{Ni}) \rightleftharpoons 2\text{H}(\text{Ni})$	[25]	0.01	0.0
	$\text{H}_2\text{O}(\text{g}) + (\text{Ni}) \rightleftharpoons \text{H}_2\text{O}(\text{Ni})$	[26]	0.10	0.0
	$\text{H}(\text{Ni}) + \text{O}(\text{Ni}) \rightleftharpoons \text{OH}(\text{Ni}) + (\text{Ni})$	[27]	5.0×10^{22}	97.9
	$\text{H}(\text{Ni}) + \text{OH}(\text{Ni}) \rightleftharpoons \text{H}_2\text{O}(\text{Ni}) + (\text{Ni})$	[28]	3.0×10^{20}	42.7
	$2\text{OH}(\text{Ni}) \rightleftharpoons \text{H}_2\text{O}(\text{Ni}) + \text{O}(\text{Ni})$	[29]	3.0×10^{21}	100.0
YSZ	$\text{O}_\text{O}^{2-} + (\chi) \rightleftharpoons \text{O}^{2-}(\chi) + \text{V}_\text{O}$	[30]	7.3×10^{12}	0.0
	$\text{H}_2\text{O}(\text{g}) + (\text{Zr}) + \text{O}^{2-}(\chi) \rightleftharpoons \text{OH}^-(\text{Zr}) + \text{OH}^-(\chi)$	[31]	1.2×10^{-4}	0.0
	$\text{OH}^-(\chi) + (\text{Zr}) \rightleftharpoons \text{OH}^-(\text{Zr}) + (\chi)$	[32]	2.0×10^{10}	97.9
	$\text{H}_2(\text{g}) + (\text{Zr}) + \text{O}^{2-}(\chi) \rightleftharpoons \text{H}^-(\text{Zr}) + \text{OH}^-(\chi)$	[33]	1.0×10^{-8}	100.0
TPB	$\text{H}(\text{Ni}) + \text{O}^{2-}(\chi) \rightleftharpoons \text{OH}^-(\chi) + \text{Ni} + \text{e}^-$	[34]	5.0×10^{12}	0.5
	$\text{H}(\text{Ni}) + \text{OH}^-(\chi) \rightleftharpoons \text{H}_2\text{O}(\text{Ni}) + (\chi) + \text{e}^-$	[35]	1.55×10^9	0.3

could be extrapolated. To our knowledge, this represents, nonetheless, the most detailed mechanism available and the best set of chemical parameters that can be garnered from the literature.

The process carried out by Goodwin was to fit the electrochemical parameters of several mechanisms to the experimental data in order to get the best agreement possible. It was observed that some mechanisms where better able to fit the experimental observations. Consequently, accurate mechanisms were promoted and inaccurate mechanisms were rejected. However, even after this process, some variations of the hydrogen spillover mechanisms were suggested as possible. Among these, the single channel hydrogen spillover has been chosen due to its simplicity and its good agreement with experimental data. Table II summarizes the mechanism and its parameters, which are those used in the current work.

Note that the pre-exponential factor along with the temperature dependency has been lumped together into the A_f constant. This is due to the lack of temperature-dependent data provided by Mizusaki et al. that, consequently, lead to a lack of temperature-dependent parametrization in the Goodwin et al. work. Further research in this field is certainly required in order to get temperature-dependent parameters.

The full mechanism used in the current work is detailed in Table II.

CO mechanism.—The mechanism described by Hanna et al.²⁵ is used for CO electrochemistry. As a remark, this mechanism does not imply any adsorbed species on the YSZ surface.

Surface Diffusion.—Surface diffusion parameters are provided in Table III. Parameters are not provided for the diffusivity of Ni vacancies as Hanna et al. computed the distribution of vacancies by a balance of active sites. This is a computationally stable approach.

In the mechanism proposed by Hanna et al. no data for the diffusion coefficient of O[−](YSZ) is provided, as it does not appear in their

equilibrium and steady-state formulations. In case it is needed, we rely on the data provided by Goodwin et al. present in Table I.

Chemistry.—The reaction mechanism detailed for CO is much simpler than that presented for H₂, as it implies a single CO adsorption reaction over Ni and a two-step electrochemical reaction at the TPB, where CO₂ is produced and released.

Even though coverage-dependent expressions were provided for the backward reactions, they have been neglected and microscopic equilibrium has been imposed as stated in Chemistry section.

The Hanna et al. mechanism departs from patterned anode experiments provided by Habibzadeh²⁰ at 700, 725, 750 and 775°C. Because Habibzadeh used the conventional approach used to measure voltage (i.e., take OCV as equilibrium) a correction on the pre-exponential factor is required according to:

$$k_f = A_f \exp\left(\frac{-E_a^f}{RT}\right) \exp\left(\beta_a \frac{zF}{RT} \eta_a\right) \quad [36]$$

where $\eta_a = \Delta\Phi_a - \Delta\Phi_{eq}$ is the anode overpotential, $\Delta\Phi_a$ is the potential difference between the different phases involved in the reaction and $\Delta\Phi_{eq}$ is the equilibrium potential difference between the different phases involved in the reaction. All the voltages are expressed in V. Reformulating Equation 25 as

$$k_f = A_f \exp\left(\frac{-E_a^f}{RT}\right) \exp\left(\beta_a \frac{zF}{RT} \Delta\Phi_a\right) \exp\left(\beta_a \frac{zF}{RT} \Delta\Phi_{eq}\right) \quad [37]$$

we can see $\exp\left(\beta_a \frac{zF}{RT} \Delta\Phi_{eq}\right)$ as a constant and thus lump it together with the pre-exponential factor A_f .

The full mechanism used is detailed in Table IV.

Thermodynamic data.—In order to use the microscopic reversibility hypothesis (18) thermodynamic data of all involved species is required. Most importantly, the garnering of the database has to be thermodynamically consistent (i.e., all the properties have to be referenced to the same state).

Thermodynamic data is garnered most preferably from the work performed by Moyer et al.¹⁷ and Goodwin et al.²² Table V summarizes the data used. Moyer provided a wide range of data for several species. An estimation of the missing properties was performed by forcing them to satisfy the values of ΔG° for every reaction, which were provided along with the kinetic parameters. Moyer data is provided for 750°C, 800°C and 850°C. Goodwin provided thermodynamically consistent data at 700°C. Because the experimental data that we will be comparing our model results to was taken at temperatures between 700°C and 800°C, thermodynamic data from both authors has been used.

Table III. Parameters for the calculation of D_i proposed by Hanna et al.²⁵

species	D_i° [m ² /s]	E_i^d [kJ/mol]
Ni		
(Ni)	-	-
CO(Ni) [†]	1.2×10^{-9}	28.87

[†]Differences in the values reported by Yurkiv et al.²³ and the ones calculated from Zhu et al.³¹ are observed, although the newest values provided by Yurkiv and co-workers²⁴ fixed this problem and provided good agreement with Zhu et al. work.

Table IV. Charge transfer mechanism for CO proposed by Hanna et al.²⁵ The reported active sites density for Ni is $\Gamma = 2.66 \times 10^{-8} \text{ kmol/m}^2$.

Reaction		$A_f^{\ddagger\ddagger}$ or γ_0 [mol, cm, s]	$E^{f\ddagger}$ [kJ/mol]	β
Ni	$\text{CO(g)} + (\text{Ni}) \rightleftharpoons \text{CO(Ni)}$	[38]	0.5	0.0
TPB	$\text{O}_\text{O}^{2-} + (\chi) \rightleftharpoons \text{O}^-(\chi) + \text{V}_\text{O} + \text{e}^-$	[39]	3.456×10^{14}	0.5
	$\text{O}^-(\chi) + \text{CO(Ni)} \rightleftharpoons \text{CO}_2 + (\chi) + (\text{Ni}) + \text{e}^-$	[40]	8.745×10^{13}	0.5

[†]Although Hanna et al.²⁵ proposed correlations for both the forward and the reverse rate, following the microscopic reversibility hypothesis stated in Electrochemical kinetics section, only the forward rate of reaction is considered.

[‡]Correction of Hanna et al.²⁵ data has been performed in order to account for the proper voltage reference.

In order to obtain the thermodynamic properties at every temperature, a linear fit to the data is performed and so a constant heat capacity is extracted. The value of C_p is calculated by two means: by fitting the values of H° and the values of S° . Good agreement between both methods is observed, except for the species present in the (χ) and (Zr) sites. In particular, there is a deviation in the values computed from S° for the species present on the electrolyte. The source of the conflict is due to the data suggested by Goodwin et al. for entropy. Interestingly, the values provided by Goodwin for H° match linearity with those provided by Moyer. In addition, by using S° values from Moyer's data only, the resulting C_p is almost the same as that provided by the full data set of H° . Finally, C_p values obtained from S° fit have been preferred when establishing thermodynamic properties of the system. The final calculated values of heat capacity that are used in this work are presented in Table VI.

Results and Analysis

H_2 electrochemical model.—As Goodwin et al.²² did, our simulation results are compared with Mizusaki et al.¹⁸ experimental results, as shown in Figures 4 and 5.

As mentioned previously the thermodynamic data considered in this work presents some bias towards the values presented by Moyer et al.,¹⁷ which could explain the differences in the open circuit voltage (OCV) presented.

Differences at the forward current (right) branch of Figure could be improved by removing the thermodynamically consistent constraint, as it would allow an extra degree of freedom to fit the reverse rate reactions. However, this would lead to a non-realistic model.

While the current trends for both forward and reverse reactions well represent those of the Goodwin et al.²² model, they are offset by an

Table V. Standard-state thermodynamic properties reported by Moyer et al.¹⁷ and Goodwin et al.²²

Author T(°C)	$H^\circ(\text{kJ/mol})$				$S^\circ(\text{J/mol/K})$			
	Goodwin 700.0	750.0	Moyer 800.0	850.0	Goodwin 700.0	750.0	Moyer 800.0	850.0
H ₂	19.9	21.4	22.9	24.5	165.3	166.8	168.3	169.7
H ₂ O	−217.8	−214.9	−212.8	−210.7	231.5	233.5	235.5	237.4
CO		−88.0	−86.4	−84.7		235.3	236.9	238.4
CO ₂		−358.7	−355.9	−353.1		270.7	273.4	276.0
O ₂	21.8	23.5	25.3	27.0	242.3	244.4	246.0	247.6
N ₂		22.3	23.9	25.6		228.9	230.5	232.0
Ar		15.1	16.1	17.2		180.4	181.4	182.3
Nickel surface								
(Ni)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H(Ni)	−32.7	−32.0	−31.2	−30.4	39.6	40.4	41.1	41.9
O(Ni)	−228.7	−228.0	−227.4	−226.8	32.4	33.0	33.6	34.2
O [−] (Ni)	−228.7	−228.0	−227.4	−226.8	32.4	33.0	33.6	34.2
O ^{2−} (Ni)	−228.7	−228.0	−227.4	−226.8	32.4	33.0	33.6	34.2
OH(Ni)	−199.7	−198.3	−196.8	−195.4	99.6	101.1	102.4	103.7
H ₂ O(Ni)	−281.6	−279.5	−277.4	−275.3	122.5	124.5	126.6	128.5
CO(Ni)		−203.5	−201.9	−200.2		157.1	158.6	160.1
CO ₂ (Ni)		−388.9	−386.3	−383.7		172.3	174.8	177.2
YSZ Surface								
(χ)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
O(χ)	−85.6	−84.7	−83.9	−83.0	139.6	149.2	150.0	150.8
O [−] (χ)	−85.6	−84.7	−83.9	−83.0	139.6	149.2	150.0	150.8
O ^{2−} (χ)	−85.6	−84.7	−83.9	−83.0	139.6	149.2	150.0	150.8
OH [−] (χ)	−173.8	−172.3	−170.8	−169.3	124.5	130.3	131.7	133.1
CO(χ)	0.0	−159.0	−159.0	−159.0	0.0	172.0	172.0	172.0
(Zr)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H [−] (Zr)	90.3	91.2	92.1	93.1	37.0	42.3	43.2	44.0
OH [−] (Zr)	−208.8	−207.3	−205.8	−204.3	124.5	130.3	131.7	133.1
Bulk YSZ								
VO	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
OO	−85.6	−84.7	−83.9	−83.0	148.4	149.2	150.0	150.8

Table VI. Calculated Cp and its correlation values.

	Fit S°		Fit H°	
	Cp(kJ/mol)	R ²	Cp(kJ/mol)	R ²
Gas				
Gas H ₂	3.08×10^{-2}	99.99%	3.06×10^{-2}	99.97%
H ₂ O	4.12×10^{-2}	99.99%	4.68×10^{-2}	99.30%
CO	3.32×10^{-2}	100.00%	3.30×10^{-2}	99.97%
CO ₂	5.68×10^{-2}	100.00%	5.60×10^{-2}	100.00%
O ₂	3.67×10^{-2}	99.74%	3.48×10^{-2}	99.99%
N ₂	3.32×10^{-2}	100.00% [†]	3.30×10^{-2}	99.97%
Ar	2.04×10^{-2}	99.97% [†]	2.10×10^{-2}	99.92%
Nickel surface				
(Ni)				
H(Ni)	1.59×10^{-2}	99.89%	1.54×10^{-2}	99.90%
O(Ni)	1.26×10^{-2}	99.95%	1.26×10^{-2}	99.85%
O ⁻ (Ni)	1.26×10^{-2}	99.95%	1.26×10^{-2}	99.85%
O ²⁻ (Ni)	1.26×10^{-2}	99.95%	1.26×10^{-2}	99.85%
OH(Ni)	2.85×10^{-2}	99.97%	2.88×10^{-2}	99.98%
H ₂ O(Ni)	4.21×10^{-2}	99.97%	4.20×10^{-2}	100.00%
CO(Ni)	3.22×10^{-2}	99.98%	3.30×10^{-2}	99.97%
CO ₂ (Ni)	5.25×10^{-2}	100.00%	5.20×10^{-2}	100.00%
YSZ Surface				
(χ)				
O(χ)	1.72×10^{-2}	99.98% [†]	1.72×10^{-2}	99.95%
O ⁻ (χ)	1.72×10^{-2}	99.98% [†]	1.72×10^{-2}	99.95%
O ²⁻ (χ)	1.72×10^{-2}	99.98% [†]	1.72×10^{-2}	99.95%
OH ⁻ (χ)	3.00×10^{-2}	99.98% [†]	3.00×10^{-2}	100.00%
CO(χ)				
(Zr)				
H ⁻ (Zr)	1.82×10^{-2}	99.96% [†]	1.86×10^{-2}	99.93%
OH ⁻ (Zr)	3.00×10^{-2}	99.98% [†]	3.00×10^{-2}	100.00%
Bulk YSZ				
VO				
OO	1.67×10^{-2}	99.95%	1.72×10^{-2}	99.95%

[†] Values obtained using Moyer et al.¹⁷ data only.

Figure 4. Polarization curves for H₂ electrochemistry with Goodwin's correlations. H₂O partial pressure has been hold fixed at $P_{H_2O} = 3000 \text{ Pa}$ and H₂ partial pressure has been varied from 1000 to 10000 Pa. Total pressure is 1 atm which has been balanced with N₂.

Figure 5. Polarization curves for H₂ electrochemistry with Goodwin's correlations. H₂ concentration has been hold fixed at $P_{H_2} = 850 \text{ Pa}$ and H₂O partial pressure has been varied from 400 to 1700 Pa. Total pressure is 1 atm which has been balanced with N₂.

Figure 6. Polarization curves for CO electrochemistry with Hanna's correlations vs Habibzadeh²¹ experimental data. Both CO and CO₂ concentrations have been hold fixed at $P_{CO} = 32677 Pa$ and $P_{CO_2} = 3267 Pa$. Total pressure is $1 atm$ which has been balanced with Ar.

unacceptably large margin. We believe this is due to the discrepancies existing in the literature regarding thermodynamic data.

CO electrochemical model.—The CO model was compared against the data provided by Habibzadeh et al.²¹ It presents the polarization curves for a fixed fuel concentration at four (4) temperature levels: 700, 725, 750 and 775°C.

As shown in Figure 6, while the polarization trends are consistent with the data there is an acute mismatch for the OCV values.

The fact that Hanna et al.²⁵ provided the forward and backward reaction rates, but did not assume microscopic reversibility, as we did, may contribute to this discrepancy.

Additional errors may arise by not accounting for the kinetics at the cathode, which are well-known to be slower than the kinetics at the anode. Even though the impact of this is very small when the cathode presents a porous structure and the anode does not, the use of a conventional LSM-YSZ cathode instead of Pt paste increases the non-suitability of the test conditions.

Hanna et al.²⁵ mentioned in their work that the surface diffusion of CO(Ni) was the rate-determining step. Consequently, differences in the surface diffusion could lead to divergences as well.

H₂-CO mixture.—A significant contribution of the current work involves analysis of H₂-CO mixture kinetics, which will include the analysis of both polarization curves and species distribution on both the anode and the electrolyte.

Cases where investigated by varying the H₂-CO mixture ratio with constant partial pressures of H₂O and CO₂ for all cases (i.e., even when only H₂ or CO were present). This was due to the constant gas composition stated in Model formulation section. N₂ was used to balance the mixture. Five (5) levels were tested for the fuel mixtures while three (3) operating temperatures were considered. A total of fifteen (15) cases were evaluated. Details of all of the parameters can be found in Table VII.

Fuel composition cases are named after the fuel fraction in the mixture (e.g., 25H₂-75CO-700 corresponds to 25% of H₂, 75% of CO at 700°C).

Polarization analysis.—Results show faster kinetics for H₂, while CO electrochemistry presents a more stable OCV. Due to the thermo-

Table VII. Test conditions for performed experiments. In parentheses is indicated the fraction of the fuel mixture (i.e., fraction of H₂ and CO over the total). The molar fraction of H₂O and CO₂ are both fixed at 3.2%, while the mixture is balanced with N₂ at 66.66%. Total pressure was fixed at $P = 101325 Pa$.

Case ID					
Fuel	T (°C)	x_{H_2}		x_{CO}	
0H ₂ -100CO	750	0.00%	(0%)	26.93%	(100%)
25H ₂ -75CO	750	6.73%	(25%)	20.20%	(75%)
50H ₂ -50CO	750	13.47%	(50%)	13.47%	(50%)
75H ₂ -25CO	750	20.20%	(75%)	6.73%	(25%)
100H ₂ -0CO	750	26.93%	(100%)	0.00%	(0%)
0H ₂ -100CO	800	0.00%	(0%)	26.93%	(100%)
25H ₂ -75CO	800	6.73%	(25%)	20.20%	(75%)
50H ₂ -50CO	800	13.47%	(50%)	13.47%	(50%)
75H ₂ -25CO	800	20.20%	(75%)	6.73%	(25%)
100H ₂ -0CO	800	26.93%	(100%)	0.00%	(0%)
0H ₂ -100CO	850	0.00%	(0%)	26.93%	(100%)
25H ₂ -75CO	850	6.73%	(25%)	20.20%	(75%)
50H ₂ -50CO	850	13.47%	(50%)	13.47%	(50%)
75H ₂ -25CO	850	20.20%	(75%)	6.73%	(25%)
100H ₂ -0CO	850	26.93%	(100%)	0.00%	(0%)

dynamic properties of both reactants and products, OCV for CO is less temperature dependent. On the other hand, CO electrochemical kinetics are slower than H₂ electrochemical kinetics.

The progressive introduction of CO in the fuel mix increases the degree to which OCV remains relatively constant, as expected. In fact, for concentrations of CO in a H₂-CO mixtures of 50% or higher, the OCV is almost constant.

As proved experimentally by Sukeshini et al.,¹⁰ the introduction of some H₂ in the CO stream increases the current density and stabilized the OCV. As Sukeshini et al. mentioned in their work, this increase in the performance can be achieved with a concentration as low as 25% of H₂ in the fuel.

Figures 7–9 show how the mixture composition affects the polarization curves at constant temperatures.

Similar to previous findings e.g. Sukeshini et al.,¹⁰ the use of H₂-CO mixtures enhances the response of the system at high temperatures. They present a more robust current production performance

Figure 7. Tafel plots for $T = 750^\circ C$.

Figure 8. Tafel plots for $T = 800^{\circ}\text{C}$.

as a function of anode overpotential compared to those presented by pure H_2 .

Differences between different compositions are smaller at higher temperatures. In particular, as it can be seen in Figure 9, after 850°C differences between H_2 and CO -rich mixtures are very small.

The improvement in performance at high temperature of CO mixtures is such that the performance predicted by H_2 - CO mixtures is even better than that predicted by pure H_2 . This could be explained by the fact that H_2 electrochemical kinetics decreases current production when working at high overpotential. This is a consequence of having less Gibbs free energy available at higher temperatures to overcome the activation energy. On the other hand, the thermodynamic potential that CO creates is higher and could thus provide more ability to overcome the activation energy for the CO kinetics.

Figure 9. Tafel plots for $T = 850^{\circ}\text{C}$.

Figure 10. Surface coverages for 100% H_2 0% CO at 750°C .

Surface analysis.—Analysis of the species distribution on the electrolyte and the electrode surfaces are performed in order to visualize the effect of the mechanisms involved.

The model produces the species fields on both the electrode and the electrolyte at every point of the i - V curve. However, for the sake of a fair comparison, all the analysis performed in this section will be at a fixed electrode-electrolyte voltage difference of -0.35V .

Figures 10–14 show the species distributions on the anode-electrolyte assembly at 750°C .

As described in CO mechanism section, desorption of CO_2 occurs directly at the TPB, while H_2O should be observed at Ni electrode through $\text{H}_2\text{O}(\text{Ni})$. For this reason, the gradient of $\text{H}_2\text{O}(\text{Ni})$ is an indicator of the hydrogen oxidation.

A detailed, temperature dependent, plot of the $\text{H}_2\text{O}(\text{Ni})$ distribution can be found in Figures 15–17.

As seen in Figures 15–17, the distribution of $\text{H}_2\text{O}(\text{Ni})$ is pretty homogeneous along the surface for all cases and, even at the vicinity of the TPB, where it is produced, the variation is small.

Figure 11. Surface coverages for 75% H_2 25% CO at 750°C .

Figure 12. Surface coverages for 50% H₂ 50% CO at 750°C.

High temperatures present a better desorption of H₂O(Ni), and consequently lower the concentration of H₂O(Ni). This is especially clear at 850°C, as seen in Figure 17. At the same time, high temperatures promote the cell kinetics and consequently enhance the rate of production of H₂O(Ni).

The concentration of H₂ enhances the concentration of H₂O(Ni) as well. In particular, a significant increase in the H₂O(Ni) coverage occurs when fuel composition is 100% H₂ - 0% CO. This may suggest an indirect effect of the presence of CO in the mix. On the other hand, even when there is no H₂ on the mix, due to the presence of H₂O on the fuel mixture, the adsorption of CO on the surface takes place. The fact that the 0% H₂ - 100% CO case presents a flat coverage along the electrode surface implies that there is no effect of the TPB on the production of H₂O(Ni).

CO(Ni) occupies most of the active sites on the electrode as shown in Figures 11–14, and presents a small concentration gradient. However, when no CO is present in the fuel (Figure 10) CO(Ni) is produced in the vicinity of the TPB and desorbed along the electrode. This involves the production of CO through the reversible Reaction 4, which

Figure 13. Surface coverages for 25% H₂ 75% CO at 750°C.

Figure 14. Surface coverages for 0% H₂ 100% CO at 750°C.

involves the consumption of e⁻, and the later desorption through Reaction 4, resulting in a net production of CO(g).

Note, however, that due to the hypothesis stated in Domain section, the gas concentration is held constant in the anode chamber, even though CO may be released into it.

On the electrode, OH⁻(χ) concentration is clearly being produced when H₂ is present in the fuel (Figures 10–13), and consumed when no H₂ is present, as seen in Figure 14. Note that OH⁻(χ) is the first step of the oxidation of H₂ by *hydrogen spillover* to H₂O. By the complexity of the reaction mechanisms for the H₂ - H₂O pair, the consumption of OH⁻(χ) could be explained by several reactions.

Figures 18–20 show more detailed plots of the OH⁻(χ) distribution on the electrolyte surface for the cases when H₂ is present.

As mentioned previously, there is a change of tendency in the OH⁻(χ) distribution depending upon whether H₂ is present in the mix or not. OH⁻(χ) is produced at the TPB when H₂ is present, but consumed when it is not. Figures 18 and 19 show how an increase

Figure 15. Detail of H₂O(Ni) distribution for $T = 750^\circ\text{C}$.

Figure 16. Detail of $\text{H}_2\text{O}(\text{Ni})$ distribution for $T = 800^\circ\text{C}$.

of the H_2 concentration in the fuel does not produce a remarkable increase on the $\text{H}_2\text{O}(\text{Ni})$ coverage.

Figure 21 shows how an increase in temperature enhances, as it was observed for $\text{H}_2\text{O}(\text{Ni})$, the desorption of $\text{OH}^-(\chi)$ from the electrolyte surface, reducing its coverage.

Discussion

A fundamental approach to the physics of multicomponent fuel reaction in an SOFC has been outlined in this work. The mechanism implies elementary mass-action kinetics at the interfaces and transport equations.

A detailed electrochemical model has been developed along with polarization and surface analysis tools. A review of existing elec-

Figure 17. Detail of $\text{H}_2\text{O}(\text{Ni})$ distribution for $T = 850^\circ\text{C}$.

Figure 18. Detail of $\text{OH}^-(\chi)$ distribution for $T = 750^\circ\text{C}$.

trochemical mechanism has been performed in order to produce the model parameters used in the current study.

Mechanism development is based upon the use of dedicated experiments which require determination of electrode-electrolyte potentials as well as exhaustive active area quantification. In addition, both transport and consistent thermodynamic properties are required in order to capture the physics appropriately.

It is worth noting that a constant gas composition has been used in this work because of very low current density and utilization operating conditions. Thus, the effect of other reactions that may occur, such as Water Gas Shift (WGS), are not taken into account. It is known that temperature affects the conversion ratio of CO to H_2 and that it could lead, eventually, to a single H_2 electroactive species. In the current, very low current-density and constant temperature case we do not expect much gas-phase chemistry to occur. However, if higher current densities are investigated or if temperatures vary significantly then the

Figure 19. Detail of $\text{OH}^-(\chi)$ distribution for $T = 800^\circ\text{C}$.

Figure 20. Detail of $\text{OH}^- (\chi)$ distribution for $T = 850^\circ\text{C}$.

resolution of a full and coupled system (i.e., that includes chemical reactions that affect local gas concentrations) is recommended.

One of the potential falsifiable hypotheses that the current model could address is the extent to which CO electrochemical kinetics in CO-H₂ mixtures contributes to voltage (for example, as opposed to WGS followed by H₂ electrochemistry). The current model and effort suggests that CO electrochemical kinetics does well contribute to creating voltage potential under the conditions investigated. But the current approach is only a step in this direction and is insufficient to prove the extent to which it contributes to voltage under practical operating conditions. The reasons why for this insufficiency are multiple: the electrochemical models are still under active development and incomplete, thermodynamic data is inconsistent, and both homogeneous and heterogeneous chemistry (e.g., for WGS) is still incomplete and inconsistent with the current model. Future work could focus on some of these issues.

Figure 21. Detail of $\text{OH}^- (\chi)$ distribution when $x\text{H}_2 = 0\%$.

Conclusions

Results show good agreement with the experimental conclusions provided previously by Sukeshini et al.,¹⁰ where concentrations on the fuel stream up to 75% CO behave similarly to those with pure H₂. Further analysis has been performed as well to understand both temperature and composition effects on the cell performance. CO has been shown to stabilize the OCV response to temperature and strengthen the H₂ response to such effect. At the same time, high temperatures have proved to improve the CO electrochemical performance compared even to hydrogen.

On the surface analysis, CO has been shown to occupy most of the active sites present in the electrode, although it does not seem to penalize the overall performance as long as there is some H₂ in the fuel stream. On the other hand, the presence of increased levels of oxidized species (i.e., H₂O and CO₂) in the anode compartment when the corresponding reducing species (i.e., H₂ and CO) is present reduces the forward rate of reaction in the TPB vicinity, penalizing the performance of the cell.

Nonetheless, the precision of the model may be improved with the use of a detailed, and validated, CO mechanism, which at this point is using a simple model.

Vogler et al.²⁷ suggested that diffusivity might be fitted (together with other kinetic parameters) to experimental data. There is a lack of detailed diffusivity parameters for most of the species involved, and thus better characterization of the diffusivity may improve results, in addition to the inclusion of coverage-depending diffusion models.

In addition, the use of validated thermodynamic properties for wider range of temperatures and species would allow an easier comparison between different mechanisms. Thermodynamic data quality and consistency could be enhanced by using statistical mechanics simulations.

Finally, there is an evident lack of experimental data for patterned anode experiments with H₂-CO mixtures, which may contribute to the understanding of the competitive kinetics involved.

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