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Kinetic Modeling of Nickel Oxidation in SOFC Anodes

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Understanding the mechanisms of performance degradation is of key importance for increasing the lifetime of solid oxide fuel cells (SOFC). The aim of this work is to achieve a deeper understanding of the processes leading to nickel oxidation at Ni/YSZ composite anodes. We present a kinetic model of chemical nickel oxidation which was integrated into a two-dimensional model of an anode-supported single cell. The feedback between nickel oxidation and cell performance was modeled by taking into account both a loss in kinetic performance (via reducing three-phase boundary length) and a reduction in gas-phase diffusivity (via porosity decrease upon solid volume expansion). The simulations allow the quantification of nickel oxide formation over time and its influence on the cell performance.

Introduction

Understanding the mechanisms of degradation is of key importance for increasing the lifetime of solid oxide fuel cells (SOFCs). All components of the SOFC (electrodes, electrolyte, interconnectors) are subject to ageing, however, with different kinetics and largely different mechanisms. This includes chemical degradation (change of chemical composition, interdiffusion of species, formation of secondary phases) as well as structural degradation (grain coarsening, loss of contact points) and thermomechanical degradation. The present work focuses on chemical degradation of nickel/yttria-stabilized zirconia (Ni/YSZ) composite anodes. In this materials system, three main modes of degradation have been identified:

- Oxidation of nickel particles during redox cycles or upon low cell voltages, leading to a coarsening of the structure (1)
- Carbon deposition during internal reforming or direct-hydrocarbon operation (2)
- Formation of bulk or surface nickel sulphides upon operation with sulfur-containing fuels (2)

We present a two-dimensional kinetic model of nickel oxidation in Ni/YSZ anodes. The simulation allows the prediction of nickel oxide (NiO) formation over time and as function of spatial position, as well as its influence on the cell performance under arbitrary operation conditions. Results are shown for different operation scenarios.

Modeling Methodology

SOFC Model

We use a model of an anode-supported single cell including gas supply channels. The two-dimensional modeling domain is illustrated in Figure 1, and main model parameters are summarized in Table I. All model equations were derived and summarized in Ref. (3). Briefly, one-dimensional channel flow (*x* dimension) is described using the Navier-Stokes conservation equations (continuity, species, momentum). One-dimensional mass transport through the MEA (*y* dimension) is described by coupled Fickian/Knudsen diffusion. Charge transport in the solid electrolyte and the electrolyte phase of the composite electrodes is described in two dimensions using Ohm's law. Anode and cathode electrochemistry is modeled using modified Butler-Volmer kinetics according to Zhu et al. (4). The results shown in this paper are calculated under the assumption of isothermal conditions at T = 1073 K. The anode is operated using humidified hydrogen with different H_2/H_2O ratios, and the cathode is operated with air. An exemplary simulated IV-curve is shown in Figure 2. The model yields a typical nonlinear behavior and performance of anode-supported SOFCs (5). The rather high performance is due to the low fuel utilization (32 % at 5 A/cm^2) assumed in the present simulations.

TABLE I. SOFC model parameters.

Cell geometry	**Value**
Anode thickness	1000 µm
Cathode thickness	20 µm
Electrolyte thickness	20 µm
Channel geometry	
Channel length	0.05 m
Channel width	0.001 m
Exchange current density	
Anode, H_2 oxidation	8.5 10^4 A/m^2
Cathode, O_2 reduction	2.8 10^4 A/m^2
Nickel oxidation kinetics (corresponding to reaction [2])	
Preexponential factor	5 10^{15} mol/Km^{3}s
Activation energy	120 kJ/mol
Initial anode composition	
Nickel content	34 Vol. %
Nickel oxide content	0 Vol. %
YSZ content	33 Vol. %
Porosity	0.33

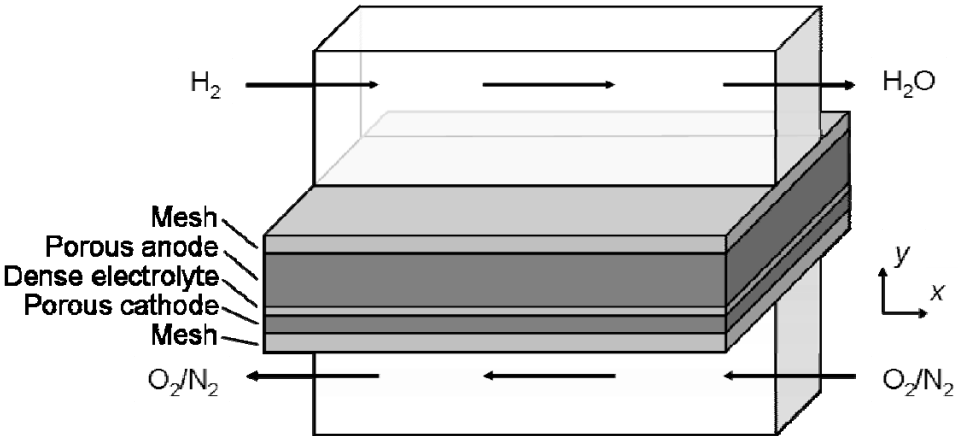

Figure 1. Two-dimensional modeling domain for the numerical kinetic simulations.

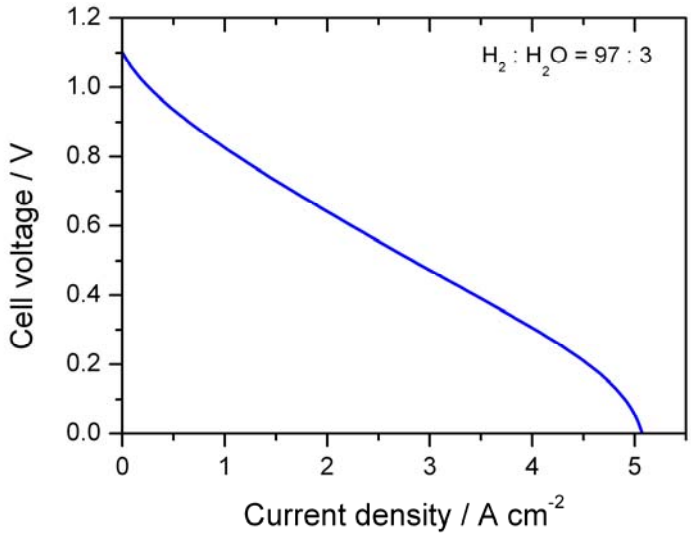

Figure 2. Simulated IV-curve of the cell model used in this study.

Nickel Oxidation

The oxidation of nickel can occur via two different pathways as illustrated schematically in Figure 3. The first one is a purely chemical reaction,

$$Ni + \tfrac{1}{2} O_2 \rightleftharpoons NiO \quad [1]$$

$$Ni + H_2O \rightleftharpoons NiO + H_2 \quad [2]$$

These reactions take place at the interface between metallic nickel and gas phase. The thermodynamic equilibrium between Ni, NiO and O_2 can be described as a function of temperature and local oxygen partial pressure. We use thermodynamic data of Ni and NiO from literature (6, 7). Thermodynamic calculations are shown in Figure 4. Thermodynamics predicts a limiting oxygen partial pressure; above this partial pressure, nickel oxide formation is thermodynamically favored, below this partial pressure nickel formation takes place. Figure 4 shows that the limiting partial pressure is a function of temperature. During SOFC operation, high oxygen partial pressures can occur if the fuel utilization is too high, causing a low H_2/H_2O ratio at some parts of the cell.

The second reaction pathway is the electrochemical oxidation of nickel taking place at the surface between the ion conductor (typically yttria-stabilized zirconia, YSZ) and the metallic nickel (cf. Figure 3),

$$Ni + O^{2-} \rightleftharpoons NiO + 2\,e^{-} \qquad [3]$$

This reaction takes place in the case of low cell voltages. This may be the case, for example, upon an interruption of the fuel supply during galvanostatic operation.

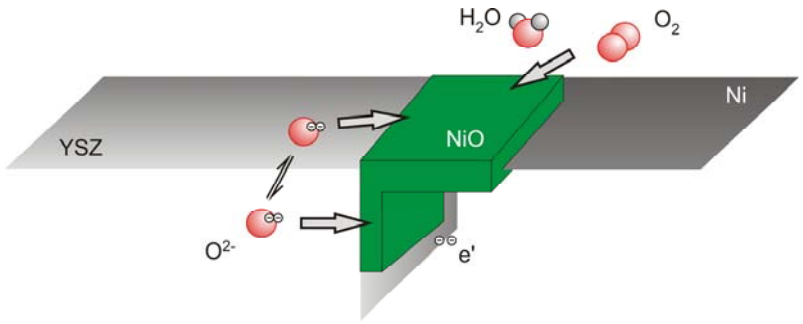

Figure 3. Schematic illustration of the reactions between Ni, YSZ and gas phase leading to oxidation of the metallic nickel. The oxidation reaction can occur at the Ni/gas interface as well as at the Ni/YSZ interface.

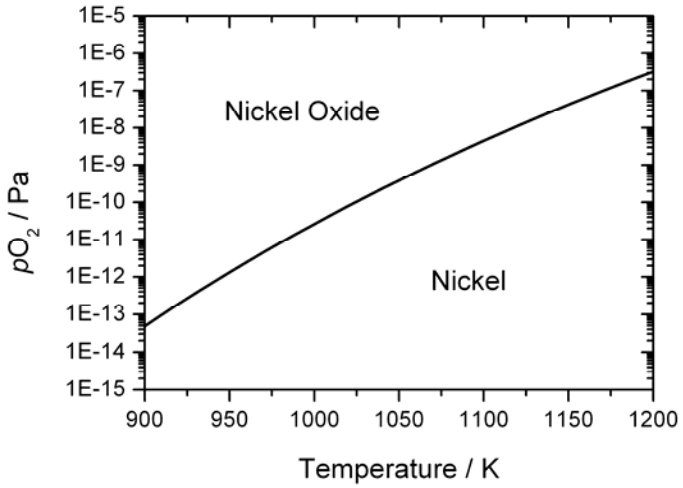

Figure 4. Thermodynamics of nickel oxidation as function of the partial pressure of molecular oxygen at the anode.

In the present study, only the first reaction pathway (chemical nickel oxidation, reaction [2]) was considered. In electrochemical equilibrium, the electrochemical potentials of O_2, H_2O and O^{2-} are identical; therefore it is sufficient to consider only one single reaction under reactions [1]-[3]. Under realistic operating conditions, however, it is likely that kinetic effects play a non-negligible role. The coupling of chemical and electrochemical nickel oxidation pathways will be subject of future investigations.

For quantifying the evolution of nickel and nickel oxide at the anode, the volume fractions of solid and pore phases are modeled as a function of spatial location inside the cell. Note that nickel oxidation is associated with a change in molar volume. We assume a four-phase-system consisting of Ni, NiO, YSZ and pore space (i.e., gas phase) and

solve for the mass density $\varepsilon\rho$ of each phase under the boundary condition of $\sum \varepsilon_i = 1$. The governing equations are given by

$$\frac{\partial \varepsilon_i \rho_i}{\partial t} = R_i \cdot M_i \qquad [4]$$

where M_i [kg/mol] is the molar mass and R_i [mol/m^{3}s] the formation rate of the solid phase i. For NiO formation (Reaction [2]), the following rate law is assumed,

$$R_{NiO} = -R_{Ni} = k_f\, \varepsilon_{Ni} - k_r\, \varepsilon_{NiO} \qquad [5]$$

where k_f and k_r are forward and reverse reaction rate constants. The forward rate constant is given by an Arrhenius expression,

$$k_f = A e^{\frac{-E_{act}}{RT}} \qquad [6]$$

where A_i [mol/Km²s] is a preexponential factor, T [K] the temperature, E_{act} [kJ/mol] the activation energy, and R the ideal gas constant, while the reverse rate constant follows from thermodynamic consistency (3) using the thermodynamic data (cf. Figure 4),

$$k_f/k_r = -\exp(\Delta G_R/RT) \quad . \qquad [7]$$

where ΔG_R is the Gibbs reaction enthalpy. Since solid YSZ is nonreactive at the investigated temperature region, R_{YSZ} is assumed to be zero.

The feedback between nickel oxidation on cell performance was modeled by taking into account both, a loss in kinetic performance and a reduction in gas-phase diffusivity. The reduction of kinetics was modeled by linearly scaling the exchange current density of the electrochemical hydrogen oxidation reaction with the volume ratio $\varepsilon_{Ni}/(\varepsilon_{Ni} + \varepsilon_{NiO})$. This simple rate law does not take into account the complex interdependence of active three-phase boundary length and nickel oxide content, however was used in the present study as first approximation. Gas-phase diffusivity is reduced because the solid volume expansion upon Ni oxidation which reduces the porosity.

Numerical Simulation

The simulations were carried out using the in-house software package DENIS (detailed electrochemistry and numerical impedance simulation) (3). In order to evaluate the chemical source terms (R_i in Equation [4]), we use the software CANTERA developed by Goodwin and co-workers (8). CANTERA is an open-source software that allows the simulation of complex reaction systems based on conveniently-structured input files. We have successfully coupled CANTERA modules (written in C++) directly to our in-house software code DENIS (written in C), making the full CANTERA functionality available during DENIS runtime. For numerical simulation, the computational domain was spatially discretized into 5 × 21 control volumes ($x \times y$ dimension).

Results and Discussion

The present model allows the simulation of chemical nickel oxidation during the operation of an SOFC at arbitrary operation conditions. In the following some particular cases are shown and discussed.

Normal Cell Operation

Figure 5 shows the temporal evolution of current and average NiO volume fraction for a voltage variation over 18 h operating time. The fuel gas contains a composition of 97 % H_2 and 3 % H_2O, which corresponds to a typical operation mixture. For four hours a constant voltage (green line) of 0.9 V was applied, and then it was linearly reduced down to 0.2 V within 2 h. At this level it was held for another 7 h and subsequently raised back to 0.9 V. As expected, lowering the voltage leads to a higher current density (blue). Nickel oxide volume fraction (black dots) increases within a few hours and decreases to its original level after increasing the voltage. Nickel oxidation is delayed relative to the voltage variation. With the parameters used in the present study, nickel oxidation occurs in a time scale of around 5 hours. Nickel oxidation leads to a reduction of current density which is due to the combined effects of electrochemical deactivation and reduction of porosity. Under the presently assumed operating conditions with low fuel utilization, NiO volume fraction does not increase about 0.4 Vol.-%. This low amount does not have a significant influence on overall cell performance.

Insufficient Fuel Supply

The nickel oxide formation in case of insufficient fuel supply to a cell (high fuel utilization) is shown in Figure 6. In this simulation the fuel gas has a content of only 5 % H_2 and 95 % H_2O, which can be the case either at the fuel outlet of the cell at high fuel utilization or if the fuel supply to the cell is interrupted. A constant voltage (green line) of 0.6 V causes a drop in current density (blue line) over a period of about 35 hours. During the same time the NiO content (black-dotted line) increases up to a volume fraction of 7.4 %, where it remains stable. The red dotted line shows the simulated current density without considering nickel oxidation. Comparing the current density with and without nickel oxidation helps to interpret the occurring effects. Diffusion limitation inside the anode causes a lack of hydrogen at the electrochemically active regions, where the water content increases even above the level of 95 %. Missing H_2 brings down the current density even when nickel is not oxidized (red-dotted line). Additionally, high water concentrations lead to NiO formation, further decreasing current density (blue line).

Spatially Resolved Evolution of Nickel Oxide Formation

Figure 7 shows the spatially resolved evolution of nickel oxide volume fraction inside the anode, after a sudden voltage variation from 0 V to 0.69 V (fuel gas mixture: 97 % H_2, 3 % H_2O). Three points of time were chosen, which correspond to the beginning (t = 1 h), the middle (t = 2 h) and the end (t = 6 h) of the oxidation process. The simulations show that nickel oxide formation starts close to the solid electrolyte on the gas inlet side of the cell. In the following it forms along the complete cell length and finally develops the highest values close to the solid electrolyte at the gas outlet side.

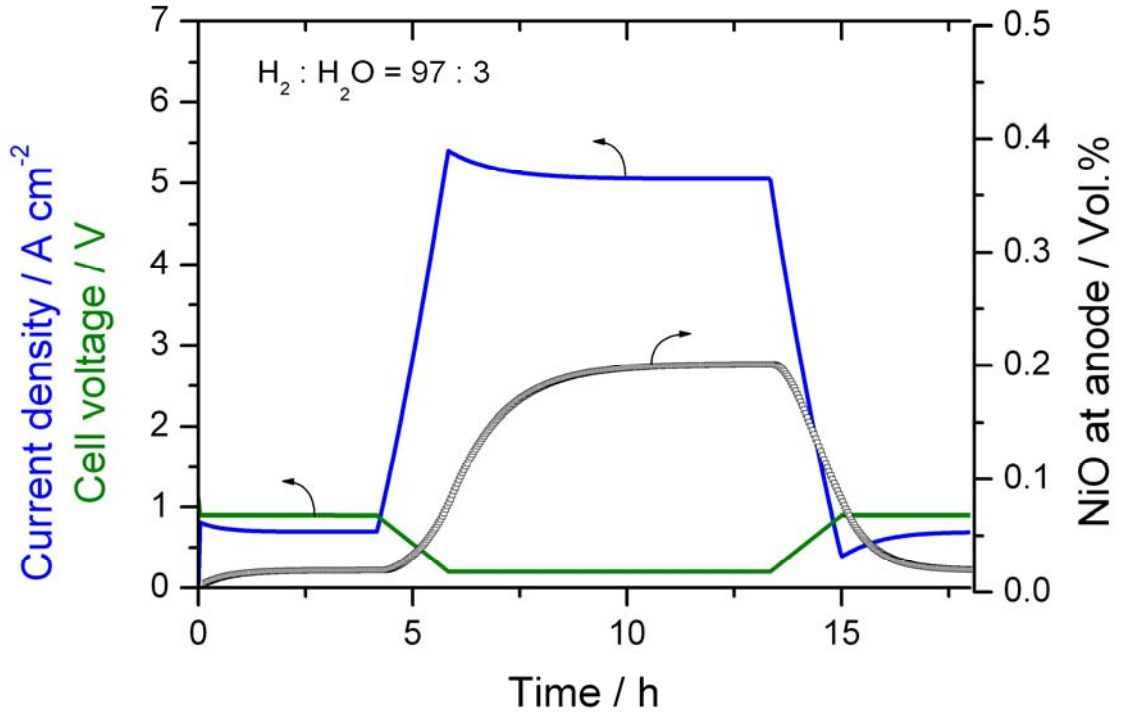

Figure 5. Formation of nickel oxide during cell operation under varying voltage.

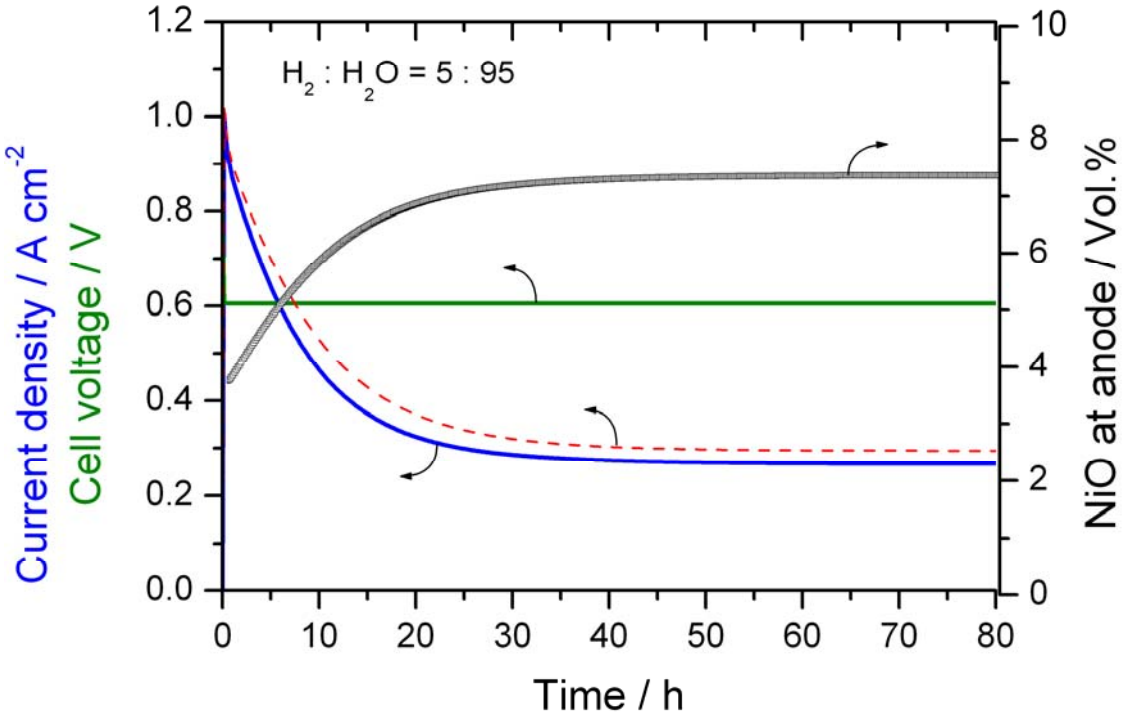

Figure 6. Formation of nickel oxide at low fuel concentrations. The red dotted line shows the simulated current density without considering nickel oxidation.

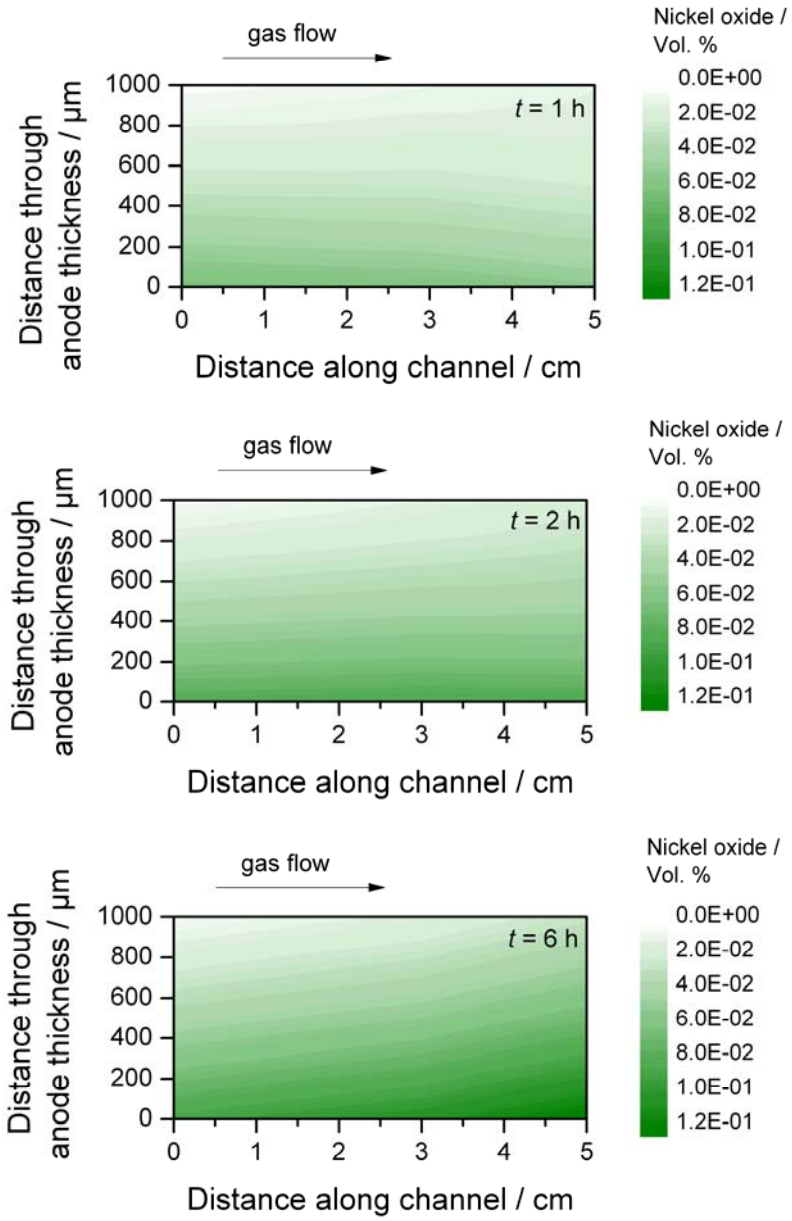

Figure 7. Evolution of nickel oxide formation inside the anode, cell operation at 0.69 V, $H_2 : H_2O = 0.97 : 0.03$.

Summary and Conclusions

A two-dimensional SOFC model incorporating nickel oxidation was presented. The model applies Butler-Volmer kinetics for electrochemical hydrogen oxidation and oxygen reduction at anode and cathode, respectively, as well as global kinetics for nickel oxidation and reduction. Thermodynamic data for Ni and NiO were taken from literature. The feedback between nickel oxidation and cell performance was modeled by taking into account both, a loss in kinetic performance (via reducing three-phase boundary length) and a reduction in gas-phase diffusivity (via porosity decrease upon solid volume expansion). The model is used to simulate the spatial and temporal evolution of NiO volume fraction and cell performance for different operating scenarios (cell voltage

cycling and insufficient fuel supply). Results show that for a sufficient fuel supply (low fuel utilization), even at low-voltage cell operation a maximum amount of only 0.2 Vol.-% NiO is formed. However, high fuel utilization or insufficient fuel supply can lead to strong oxidation and thus a reduction in the cell performance. The model allows identifying the regions and timescale of NiO formation and therefore enables the development of optimized operating strategies for avoiding degradation due to nickel oxidation.

Acknowledgments

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