IMPEDANCE SIMULATIONS
OF SOFC PATTERNED AND CERMET ANODES
FROM DETAILED ELECTROCHEMICAL MODELS

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ABSTRACT
A new computational approach for simulating impedance spectra of solid oxide fuel cells from detailed physicochemical models is presented. It is based on transient numerical simulations (TNS) of the dynamics of the electrochemical system when a periodic variation of overpotential is imposed. Impedance is calculated, in the time domain maintaining the full nonlinearity of the system. The method is used to predict impedance of SOFC Ni/YSZ patterned anodes operated with H2/H2O based on a six-step surface electrochemical reaction model taken from literature. Impedance of Ni/YSZ cermet anodes is simulated from coupled models of surface electrochemistry, diffusive porous gas-phase transport, and electronic/ionic conductivity of metal and electrolyte. The simulation results qualitatively agree with literature experimental data. The study shows, however, that the models are not sufficiently detailed for a quantitative description of anodic behavior.

INTRODUCTION
Electrical impedance spectroscopy (EIS) has proven a powerful tool in investigating electrochemical and transport processes in solid oxide fuel cells (SOFCs) (1). Impedance spectra are most commonly interpreted using equivalent circuit models (2). This interpretation, however, allows only limited insight into the fundamental physical or chemical processes, not only due the ambiguity of equivalent circuits, but also because of their global nature, averaging over all microscopic processes. The concept is therefore mostly used for a phenomenological, while still useful description of electrochemical systems.

Alternatively, SOFC electrochemistry has been modeled with a detailed description of the chemical kinetics (rate equation description of chemical and charge-transfer reactions) and transport processes (fluid-dynamical description of convection and diffusion). While CFD-type models have been widely employed on a cell- and stack-level scale, they usually apply simplified, global descriptions of electrode processes. They can be used for predicting polarization curves, but they are not able to describe the dynamical behavior during impedance measurements.

Even if detailed-chemistry models are available, impedance simulations require the use of elaborate numerical algorithms. Gauckler and co-workers have successfully used state-
space modeling (SSM) for impedance simulations of SOFC cathodes and anodes (3,4). Their method is based on linearization of the governing equations, subsequent Laplace transformation, and impedance calculation in the frequency domain. We present and apply an alternative approach based on transient numerical simulation (TNS) of the governing equations (5,6), where impedance is calculated in the time domain maintaining the full nonlinearity of the system.

**TRANSIENT NUMERICAL SIMULATION METHODOLOGY**

The response of an electrochemical system to alternating current excitation is due to the coupling of the dynamical properties of the governing processes. We apply the following methodology for impedance simulations:

1) A model of the electrochemical system is developed. In this paper we present models for SOFC anodes consisting of detailed surface electrochemistry (rate equation description), diffusive porous gas-phase transport (Stefan-Maxwell multi-component transport) and conductive properties (Ohm's law). Details are given in the next sections.

2) A consistent mathematical representation is set up that describes the dynamical properties of the model in the form of differential-algebraic equations (DAE),

\[
\frac{dx}{dt} = f(x,t), \quad 0 = g(x,t),
\]

where [1] is a system of ordinary differential equations, [2] is a system of algebraic equations, \( x \) is a vector of the state variables (species concentrations, temperature, density, overpotential \( \eta \), current \( i \)) and \( t \) is the time. For chemical reactions, \( x \) represents the species concentrations, and the equation system [1] are the rate equations. For transport processes, [1] is some form of the Navier-Stokes equations, where the partial spatial derivatives of the right-hand side \( f \) are eliminated through spatial discretization techniques. Electrical properties (Ohm's law) are represented in the form of algebraic equations [2].

3) A harmonically varying overpotential \( \eta \) is imposed to the system as boundary condition,

\[
\eta(t) = \eta_{\text{steady}} + \eta_{\text{var}} \sin(\omega t),
\]

where \( \nu = \omega/2\pi \) is the alternating current excitation frequency. This approach represents a numerical experiment of impedance measurements with frequency response analyzers.

4) For impedance simulations, the equation system [1]-[2] is time-integrated for one or several periods \( \tau = 1/\nu \). This requires efficient numerical methods that can handle the stiff equation system and the boundary condition [3]. We use the implicit extrapolation solver LIMEX (7). Time-integration yields a transient numerical
representation of all state variables including the Faradaic current \( i_F(t) \) within the simulated time periods. Given \( \eta(t) \) (eq. [3]), the calculation of the Faradaic impedance \( Z_f \) is straightforward following the method used in frequency response analyzers (2),

\[
Y_f' (\omega) = \frac{2}{\eta_{var}} \int_{-\infty}^{\infty} i_F(t) \sin(\omega t) dt ,
\]

\[
Y_f'' (\omega) = \frac{2}{\eta_{var}} \int_{-\infty}^{\infty} i_F(t) \cos(\omega t) dt ,
\]

\[
Z_f(\omega) = Y_f^{-1}.
\]

For calculating the steady-state polarization of the electrochemical system, \( \eta_{var} \) is set to zero and the equation system [1]-[2] is integrated to a steady state by running LIMEX to sufficiently long integration times.

SOFC PATTERNED ANODES

Ni/YSZ Patterned Anode Electrochemistry Model

The reaction mechanisms for the SOFC \( \text{H}_2 \) oxidation proposed by different authors vary considerably, not only in their degree of simplification, but also in the general reaction path way (4,8-12). Our model is based on the mechanism proposed by Bieberle and Gauckler (4) for \( \text{H}_2 \) oxidation on a Ni/YSZ patterned electrode at \( T = 973 \text{ K} \). We find their mechanism superior to other proposed literature mechanisms due to both, its consistency since it represents a complete reaction pathway, and its basis on surface physical chemistry data.

**Charge-transfer.** A one-step charge-transfer reaction of oxygen ions from the electrolyte surface to the Nickel surface is assumed:

\[
\text{O}^{2-}_{\text{YSZ}} + \text{Ni} \rightleftharpoons \text{Ni}^{2+} + \text{YSZ} + 2e^{-} \text{ (electrode)},
\]

where \( [\text{Ni}] \) means a free surface site. The surface concentrations of oxygen ions and free sites on the YSZ are assumed constant (fast oxygen ion surface/bulk exchange reactions) and are included into the rate constants \( k_{\pm 1} \). The Faradaic current density \( i_F \) (current per area) is given by

\[
i_F(t) = zF \Gamma f_{geo} \left( k_1(t) \theta_{\text{Ni}}(t) - k_{-1}(t) \theta_{\text{o}}(t) \right) ,
\]

\[
k_1(t) = k_1^0 \exp \left( \frac{-F}{RT} \eta(t) \right) ,
\]

\[
k_{-1}(t) = k_{-1}^0 \exp \left( (1 - \alpha) \frac{-F}{RT} \eta(t) \right) ,
\]

where \( z \) is the number of electrons transferred, \( \Gamma \) is the density of surface sites, \( \theta \) are the nickel surface coverages, \( \alpha \) is the symmetry factor, and \( F, R, T \) have their usual meaning.
\( \eta \) is given by [3]. The rate coefficients \( k^0_{\pm 1} \) are calculated from the thermodynamic consistency condition that \( i \) must vanish for \( \eta = 0 \). They can be expressed as function of a charge-transfer resistance \( R^0_{ct} \) and the equilibrium surface coverages \( \theta^0 \) according to (6):

\[
k^0_i = \frac{RT}{z^2F^2T} \frac{1}{\theta^0_{Ni} R^0_{ct}} \quad k^0_{-i} = \frac{RT}{z^2F^2T} \frac{1}{\theta^0_{O} R^0_{ct}} \quad [11]
\]

In the patterned anode model assumed here, only the nickel surface is available for reaction. The Faradaic current therefore needs to be normalized with a dimensionless geometrical factor \( f_{\text{geo}} \) defined as the ratio of available reaction surface area over total macroscopic electrode area.

**Surface reactions.** We assume a hydrogen oxidation mechanism consisting of the following Langmuir-Hinshelwood type surface reaction mechanism taking place on the nickel surface:

\[
\begin{align*}
\text{ONi} + \text{H}_2\text{O} \leftrightarrow k_1 \text{OH} + [\text{Ni}] \\
\text{ONi} + \text{H}_2 \leftrightarrow k_2 2 \text{OH} + [\text{Ni}] \\
\text{OH} + \text{H}_2 \leftrightarrow k_4 \text{H}_2\text{O} + [\text{Ni}] \\
\text{H}_2\text{O}(\text{gas}) + [\text{Ni}] \leftrightarrow k_5 \text{H}_2\text{O} + [\text{Ni}] \\
\text{H}_2(\text{gas}) + [\text{Ni}] \leftrightarrow k_6 \text{H}_2 + [\text{Ni}] \quad [12-16]
\end{align*}
\]

Reactions [12]–[14] represent surface reactions between the chemisorbed neutral O, H, OH and H\(_2\)O species. [15] and [16] represent adsorption/desorption reactions of H\(_2\)O and H\(_2\) from/to the gas phase. Values for the reaction rates \( k_{\pm 1} \) at 973 K can be estimated from surface science literature (4).

**Electrical double layer and electrolyte resistance.** The electrical double layer at the nickel/YSZ interface, and the electrolyte resistance both can have a large influence on the impedance response of the system. We include these effects in a global way by calculating the total impedance \( Z \) of an \( R_\text{el}(C_{\text{dl}}Z_F) \) equivalence circuit, where \( Z_F \) is the Faradaic impedance calculated from the detailed electrochemistry model. This approach is reasonable for patterned electrodes, where it can be assumed that the complete three-phase boundary line and the Ni/YSZ interface are subject to the same electrical potentials. Values for \( R_\text{el} \) and \( C_{\text{dl}} \) can be estimated from equivalent circuit models of patterned electrodes (8), where it was observed that \( C_{\text{dl}} \) depends on \( \eta \). We found that this dependence has to be included into simulations for good agreement with experimental data.

**Mathematical Representation and Model Parameters**

The dynamics of the SOFC patterned anode system (reactions [7], [12]–[16]) is described by four rate equations for the four surface species' coverages \( \theta_{\text{H}} \), \( \theta_{\text{OH}} \), \( \theta_{\text{H}_2\text{O}} \), \( \theta_{O} \) (cf. eq. [1])
and Ref. (6)). The fraction of free nickel sites \( \theta_{\text{ Ni}} \) follows from the consistency condition that the total coverage plus free nickel sites must sum up to unity. The Faradaic current is calculated using eq. [8]. The parameters entering the patterned anode model are given in Table 1. They are obtained by taking an estimate from surface science literature and subsequently performing a parameter optimization (6) simultaneously on the following experimental data from Bieberle and Gauckler (8): Impedance (|Z| and \( \phi \) vs. \( \nu \)) at 0 and 200 mV, polarization resistance at various overpotentials, hydrogen and water concentrations (cf. Figs. 2 and 3).

Table 1: Ni/YSZ patterned anode model parameters. *Free fit parameter. a Ref. (8). b Follows from \( R_{\text{ct}} \). c Surface science data, Ref. (4). d From solid nickel density.

| Parameter | Value |
|-----------|-------|
| \( f_{\text{geo}} \) | 0.14 |
| \( \Gamma \) | 3.2 \times 10^{-9} \text{ mol cm}^{-2} |
| \( \rho_{\text{H}_2} \) | 5 \times 10^{4} \text{ Pa} |
| \( \rho_{\text{H}_2} \) | 1.5 \times 10^{4} \text{ Pa} |
| \( T \) | 973 K |
| \( C_{\text{dl}} (0 \text{ V}) \) | 6 \times 10^{-5} \text{ F/cm}^{2} |
| \( C_{\text{dl}} (0.2 \text{ V}) \) | 1.7 \times 10^{-4} \text{ F/cm}^{2} |
| \( R_{\text{ct}} \) | 1 \Omega \text{ cm}^{2} |
| \( \alpha \) | 0.5 |
| \( k_{1} \) | 5 \times 10^{2} \text{ s}^{-1} |
| \( k_{1} \) | 1.8 \times 10^{10} \text{ s}^{-1} |
| \( k_{2} \) | 2 \times 10^{11} \text{ s}^{-1} |
| \( k_{3} \) | 4 \times 10^{10} \text{ s}^{-1} |
| \( k_{4} \) | 9 \times 10^{4} \text{ s}^{-1} |
| \( k_{5} \) | 9 \times 10^{4} \text{ s}^{-1} |
| \( k_{6} \) | 1 \times 10^{4} \text{ s}^{-1} |
| \( \theta_{\text{OH}} \) | 0.14 |
| \( \theta_{\text{H}_2} \) | 0.197 |
| \( \theta_{\text{O}} \) | 0.182 |
| \( \theta_{\text{H}} \) | 0.160 |

Results and Discussion

Fig. 1 shows the results of the transient numerical simulation technique applied to the patterned anode model. The periodical variation of the state variables under the driving force of the varying overpotential (eq. [3]) can be fully reproduced using the transient simulation technique.

Figure 1. Transient numerical simulation of the patterned anode system at \( \eta_{\text{steady}} = 0 \) and 200 mV, \( \eta_{\text{var}} = 10 \text{ mV}, \nu = 10 \text{ Hz} \). Model parameters are given in Table 1.
The impedance calculated from the transient results is shown in Fig. 2 together with the experimental data [8] the model parameters were fitted to. There is qualitative agreement. The simulated impedance spectra show two processes: the low-frequency process can be attributed to surface chemistry [6], while the high-frequency process is due to the double layer capacitance. Large discrepancies between simulation and experiment are observed in the phase angle at low frequencies, indicating that either the low-frequency process is not simulated correctly or that there are additional low-frequency processes (e.g. diffusion processes) not included in the current model.

![Figure 2. Simulated and experimental (8) impedance of SOFC patterned anodes at \( \eta_{\text{steady}} = 0, 200 \text{ mV} \) and \( \eta_{\text{var}} = 10 \text{ mV} \). Model parameters are given in Table 1.](image)

Fig. 3 compares the simulated and experimental polarization resistance (defined in the simulations as \( R_{\text{pol}} = |Z(10^{-5} \text{ Hz})| \)) in dependence on overpotential and gas composition. Again, the simulation is able to reproduce the experimental data at least qualitatively. It should be noted that the catalytic effect of increasing water partial pressure is predicted. This effect is often interpreted as catalytic process on the YSZ surface [8]; however, YSZ surface processes are not included in the current model at all. Instead, this effect can be interpreted as a consequence of the \( \text{O} + \text{H}_2\text{O} \) surface reaction [13], representing a second \( \text{O} \rightarrow \text{OH} \) pathway besides the \( \text{O} + \text{H} \) reaction [12].

![Figure 3. Simulated and experimental (8) electrochemical performance of SOFC patterned anodes. Model parameters are given in Table 1.](image)

The model was fitted to experimental data using five free parameters. This is a relatively small number, as the optimized model allows reproducing a range of experimental
conditions. Equivalent circuit models, in contrast, require separate parameter fits for each experimental condition, leading to a larger total number of free parameters.

Despite the qualitative agreement between simulation and experiment, the results show that the patterned anode model needs further improvement. YSZ surface reactions and surface diffusion processes may have an important influence, and the double layer capacitance is only included in a global way. Furthermore, the model parameters were validated for $T = 973$ K only. These issues have to be subject of future investigations. Still, in order to demonstrate the applicability of our modeling and simulation approach to porous electrodes, we will apply the surface model for SOFC cermets operated under similar conditions.

**SOFC CERMET ANODES**

**Ni/YSZ Cermet Anode Model**

Porous cermets consist of a three-dimensional network of electrode, electrolyte and open pores. Transport properties of reactants/products in the gas-phase and of charge carriers in the solid phases are correlated to the microstructure in a complex way. We apply our simulation approach to state-of-the-art models of these processes (13-15). A homogenized approach is applied, i.e. properties are described by effective, macroscopic parameters.

**Electrochemistry.** We assume that the charge-transfer and surface chemical reactions are identical in cermets compared to patterned anodes and can be described using the same kinetic parameters. The available reaction surface, however, now depends on the microstructure. The Faradaic current density (now in current per volume) can be expressed as

$$i^F_F(t, z) = z F \Gamma A_p \left( k_i(\eta(t, z)) \theta_{Ni}(t, z) - k_{-1}(\eta(t, z)) \theta_{O}(t, z) \right), \quad [17]$$

where $A_p$ is the reaction surface area (area per volume) which can be expressed as a product of the three-phase boundary (tpb) length $l_{tpb}$ (length per volume) and the active width of the surface from the tpb line $w_{active}$ (length). Current, overpotential, reaction rates and surface coverages depend on the position $z$ within the cermet anode, where we define $z = 0$ at the electrolyte and $z = d_{mode}$ at the electrode/gas-phase interface.

Note that the electrochemical kinetic parameters were validated for a temperature of 973 K only (previous section). Cermet anode simulations using this model are so far restricted to this temperature.

**Electric and ionic conductivities.** When an external total overpotential $\eta_{tot}$ (i.e., measured using a reference electrode) is applied to a cermet electrode, the coupling of electric and ionic conductivity properties with the electrochemistry will lead to a characteristic distribution of local overpotential versus electrode thickness. As the electrolyte (YSZ) resistance is several orders of magnitude higher than the electrode (Ni) resistance, electrochemical activity is usually assumed to be restricted to a small spatial extent close to the solid electrolyte, referred to as “active electrode thickness”.

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The resistance of Nickel and YSZ are modeled using Ohm’s law for each component,

\[ \frac{d\phi}{dx} = \rho i \quad , \tag{18} \]

where \( \phi \) is the electrical potential and \( \rho \) the resistivity. The two materials are coupled through the Faradaic current \([17]\). The following expression for the \( z \) dependence of \( \eta \) can be derived \((13,14)\):

\[ \frac{d^2 \eta}{dz^2} = (\rho_{\text{Ni}} + \rho_{\text{YSZ}}) j^V \quad . \tag{19} \]

**Porous gas-phase transport.** In the hydrogen oxidation reaction, each mole of reactant gives one mole of product. It can therefore be assumed that there are no pressure gradients within the cermet, and diffusion is the only gas-phase transport mechanism \((16)\). Multi-component continuum diffusion of \( i \) species is described by the Stefan-Maxwell equation,

\[ \nabla n_i = \sum_{j=1}^{n} \frac{x_i J_j - x_j J_i}{D_{ij}} \quad , \tag{20} \]

where \( n_i \) are the gas-phase species concentrations, \( J_i \) the diffusive fluxes, and \( x_i \) the mole fractions. We apply Bosanquet binary diffusion coefficients \( D_{ij} \) \((16)\) which include Knudsen and continuum diffusion mechanisms (the latter calculated using Fuller’s rule \((15)\)). They are corrected for the porosity/tortuosity ratio of the porous electrode structure. We assume ternary diffusion (H\(_2\), H\(_2\)O, and an inert species) and invert eq. \([20]\) to yield diffusive fluxes in dependence of concentrations of all species.

**Electrical double layer.** The electrical double layer is modeled as for the patterned anode using a global \( R_d(C_dZ_d) \) equivalence circuit. For porous anodes, however, this approach is clearly oversimplified, as the capacitive current will contribute to the spatially inhomogeneous electrical behavior (eqs. \([18]\) and \([19]\)). A more detailed double layer model will be the subject of future investigations.

**Mathematical Representation and Model Parameters**

The spatial dimension \( z \) along the cermet electrode thickness is discretized using a finite volume approach for the governing equations \([19]\) and \([20]\) containing spatial derivatives. For each volume, this leads to four ordinary differential equations for the surface species, three for the gas phase species, and algebraic equations for the overpotential.

The cermet anode model parameters are summarized in Table 2. The structural parameters are estimated for anodes investigated by Holtappels et al. \((11,17)\). \( A_f \) is optimized to yield best agreement of simulated polarization curves with experimental data. Surface kinetic parameters are taken from Table 1.
Table 2. Ni/YSZ cermet anode parameters. *Free fit parameter. a Ref. (17). c Ref. (11). c Estimated from micrograph shown in Ref. (11).

| Parameter | Value |
|-----------|-------|
| $T$ | $^{a}993$ K |
| $P_{\text{H}_2}$ | $^{a}4.8 \times 10^5$ Pa |
| $P_{\text{H}_2O}$ | $^{a}4.1 \times 10^4$ Pa |
| $P_{\text{Ar}}$ | $^{a}4.8 \times 10^4$ Pa |
| $\rho_{\text{Ni}}$ | $1.5 \times 10^{-6}$ $\Omega$ m |
| $\rho_{\text{YSZ}}$ | 2 $\Omega$ m |
| $A_{\text{F}}$ | $^{*}1.3 \times 10^6$ $\text{m}^2$/m$^2$ |
| $C_{\text{dl}}$ | $^{b}3.1 \times 10^{-3}$ F/cm$^2$ |
| $R_e$ | $^{b}0$ |
| $d_{\text{Anode}}$ | $^{c}60$ $\mu$m |
| porosity | $^{c}0.3$ |
| tortuosity | $^{c}3.5$ |
| mean pore dia. | $^{c}10^{-6}$ m |

**Results and Discussion**

The simulated d.c. polarization behavior of the cermet anode is shown in Fig. 4 together with the experimental data (17) the model parameters were optimized to. The simulation reproduces the anodic polarization behavior very well. This is remarkable as the electrochemistry model is taken without modification from patterned anodes. The cathodic branch is not reproduced correctly; this may be reasonable given that no cathodic data were available for the patterned anodes. Fig. 4 also shows the simulated variation of overpotential, current and gas pressures along the porous electrode thickness for an overpotential of 200 mV. The variation of these parameters along the electrode is only small, and the complete electrode thickness is electrochemically active for this relatively thin (60 $\mu$m) electrode.

Figure 4. Simulated and experimental (17) polarization behavior of SOFC cermet anode and variation of state variables along electrode thickness. Model parameters are given in Tables 1 and 2.

Calculated impedance spectra are shown in Fig. 5 where they are compared to experimental impedance data (11). There is considerable disagreement between simulation and experiment. The simulation predicts two relaxation process (electrochemistry and double layer capacitance), while the experimental data show at least three processes. Thus, while Fig. 5 generally demonstrates the applicability of the transient numerical simulation approach presented in this paper, it shows that the cermet anode model used is not adequate. In particular, porous gas-phase diffusion and electrical conductivity, both included in the model, seem to have no significant influence on the impedance response of this cermet anode.
SUMMARY AND CONCLUSIONS

This paper presents an advanced computational approach for impedance calculations based on detailed electrochemical models. Impedance is calculated in the time domain after transient numerical simulation of the dynamics during a.c. excitation. The approach was applied to models of SOFC patterned and cermet anodes. The comparison with experimental data yielded good agreement for the steady-state polarization, reasonable agreement for patterned anode impedance, and considerable disagreement for cermet anode impedance. The study thus shows that the models used are only an incomplete description of the processes taking place in SOFC anodes.

REFERENCES

1. E. Ivers-Tiffee, A. Weber, and H. Schichlein, in Handbook of fuel cells - fundamentals, technology and applications, W. Vielstich, A. Lamm, and H. A. Gasteiger, Editors, p. 220, John Wiley & Sons, Chichester, (2003).
2. J. R. MacDonald, Editor, Impedance spectroscopy. Emphasizing solid materials and systems. John Wiley & Sons, New York, (1987).
3. A. Mitterdorfer and L. J. Gauckler, Solid State Ionics, 117, 187 (1999).
4. A. Bieberle and L. J. Gauckler, Solid State Ionics, 146, 23 (2002).
5. W. G. Bessler and J. Warnatz, in 6th European Solid Oxide Fuel Cell Forum Proceedings, M. Mogensen, Editor, p. 754, Lucerne, Switzerland, (2004).
6. W. G. Bessler, Solid State Ionics, submitted, (2004).
7. P. Deuflhard, E. Hairer, and J. Zugck, Num. Math., 51, 501 (1987).
8. A. Bieberle, L. P. Meier, and L. J. Gauckler, J. Electrochem. Soc., 148, A646 (2001).
9. J. Mizusaki, H. Tagawa, T. Saito, T. Yamamura, K. Kamitani, K. Hirano, S. Ehara, T. Takagi, T. Hikita, M. Ippomatsu, S. Nakagawa, and K. Hashimoto, Solid State Ionics, 70/71, 52 (1994).

10. A. S. Ioselevich and A. A. Komyshev, Fuel Cells, 1, 40 (2001).

11. P. Holtappels, I. C. Vinke, L. G. J. de Haart, and U. Stimming, J. Electrochem. Soc., 146, 2976 (1999).

12. S. Primdahl and M. Mogensen, J. Electrochem. Soc., 144, 3409 (1997).

13. J. Divisek, R. Jung, and I. C. Vinke, J. Appl. Electrochem., 29, 165 (1999).

14. S. H. Chan and Z. T. Xia, J. Electrochem. Soc., 148, A388 (2001).

15. B. Todd and J. B. Young, J. Power Sources, 110, 186 (2002).

16. B. Todd, in 2nd International conference on heat transfer, fluid mechanics and thermodynamics, Victoria Falls, Zambia, (2003).

17. P. Holtappels, L. G. J. de Haart, and U. Stimming, J. Electrochem. Soc., 146, 1620 (1999).