STATE-SPACE MODELLING OF METAL ELECTRODES IN SOLID STATE ELECTROCHEMISTRY

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ABSTRACT

Adequate data and models describing the micro-kinetics of metal electrodes in high temperature electrochemical devices are still pending. A general framework is provided for modelling reaction mechanism in state-space form. Structural investigation, computer implementation, and digital simulation of reaction models is illustrated by a first-order mechanism describing the Pt, O$_2$|YSZ system. Dissociative adsorption of oxygen on Pt, surface diffusion, and electrochemical reduction of adsorbed oxygen near the triple phase boundary line is considered. The concepts could be equally well applied to metal, H$_2$|YSZ systems.

INTRODUCTION

Electrode reactions at noble metal electrodes in solid state electrochemical devices involve a number of elementary reactions. Insight and understanding of electrode micro-kinetics is decisive for the further development of applications such as solid oxide fuel cells, oxygen sensors, or ion-transport membranes. In the classical approach of electrode modelling, mass and charge balances are specified. Steady-state current-overpotential curves are obtained by evaluating the charge balance equation at the respective operating points (1,2). Recently, an approach often used in aqueous electrochemistry (3) has been employed for the development of impedance expressions of electronically conducting electrodes on solid oxide electrolytes (4-6). This method is based on a Taylor expansion of the charge balance equation. But the previously mentioned methods suffer from the limitations that different representations are necessary to describe the static and dynamic electrode behaviour. In addition, relatively complicated expressions are obtained for the impedance even for simple reaction mechanism and the method does not enable to treat complicated systems including diffusion processes.

The purpose of the present work was to provide a method which overcomes these limitations. A general framework for identification of electrochemical reac-
tion mechanisms is given. Structural investigation, implementation, and simulation of models is illustrated by a simple first-order mechanism describing the Pt, O$_2$|YSZ system. The current presentation does not assume that the reader is familiar with digital simulation, but a basic acquaintance with control theory may be helpful. We will give a more detailed account of this subject in forthcoming publications (7,8).

THEORY

Main Hypotheses

We assume that the solid electrolyte/electrode interface can be considered as a dynamic system (Fig. 1). The voltage across the interface is the input quantity and the current is the output quantity of the system. The concentrations of adsorbed species are the state variables. Therefore, the dynamic properties can be fully described by the transfer function of the system. Microstructural data, such as the length of the triple phase boundary (tpb), or the pore size are obtained from SEM and/or AFM measurements. Adsorption and surface diffusion data are obtained from the literature. Reactions on the solid electrolyte surface are neglected. The electrochemical rate constants are supposed to be exponentially dependent on the overpotential $\eta$ (9).

Mathematical Realization

A dynamic system can by described in state-space form:

$$\dot{x}(t, p) = f(x(t, p), u(t), t; p), \quad x_0 = x(t_0, p) \quad [1]$$

$$y(t, p) = g(x(t, p); p) \quad [2]$$

where $x(t) \in \mathbb{R}^n$ is the vector of state variables; $u(t) \in \mathbb{R}^m$ is the input vector; $y(t) \in \mathbb{R}^p$ is the output vector; $p$ is the vector of the unknown parameters. In heterogeneous electrochemistry we mainly have $I_F(t, p) = y(t, p)$ and $\eta(t) = u(t)$, where $I_F$ is the Faradaic current and $\eta = E - E_{eq}$ is the deviation from the equilibrium potential $E_{eq}$. The vector $x(t, p)$ contains the unknown concentrations of adsorbed intermediate species. Linearisation of this equation system for small deviations $\delta$ around a steady-state operating point gives (see any common textbook about systems or control theory):

$$\delta \dot{x}(t, p) = A(p)\delta x(t, p) + B(p)\delta \eta(t)$$

$$\delta I_F(t, p) = C(p)\delta x(t, p) + D(p)\delta \eta(t) \quad [3]$$
where \( A(p), B(p), C(p), \) and \( D(p), \) are the system matrices (Jacobi matrices) describing the system properties entirely.

An equivalent representation of the state-space description can be obtained by Laplace transforming Eq. [3] with \( x_0 = 0 \) (where we left out the \( \delta \)):

\[
I_F(s, p) = Y_F(s, p) \eta(s),
\]

where

\[
Y_F(s, p) = C(sI - A)^{-1}B + D,
\]

\( s \) is the Laplace variable, and \( I \) is the identity matrix. The complex function \( Y_F(s = jo) \) is the frequency response (Faradaic admittance) \( (7), \) \( |Y_F(j\omega)| \) is the magnitude and \( \arg\{Y_F(j\omega)\} \) is the phase of \( Y_F(j\omega) \). Note that electrochemical impedance spectroscopy is normally carried out by imposing an alternating voltage across the interface, therefore measuring the admittance rather than the impedance.

**Some Properties of \( Y_F(s) \)**

From Eq. [3] and the definition of the charge transfer resistance:

\[
1/R_t = \left( \frac{\partial Y_F}{\partial \eta} \right)_x = D = \lim_{\omega \to \infty} Y_F(j\omega)
\]

we obtain after some elementary algebraic transformations that

\[
Z_F(j\omega) = Y_F(j\omega)^{-1} = R_t \left( 1 - \frac{R_t Y_\theta(j\omega)}{1 + R_t Y_\theta(j\omega)} \right)
\]

where \( Y_\theta(j\omega) = (C(j\omega I - A)^{-1}) + B \). The polarization resistance \( R_p \) is obtained as:

\[
\frac{1}{R_p} = Y_F(0) = D - CA^{-1}B.
\]

From Eq. [6] to Eq. [8] it is readily seen that \( Z_F(j\omega) \) is limited by \( R_t \) at high frequencies and by \( R_p \) at low frequencies. The frequency response in between these limits is given by the fraction within the brackets in Eq. [7]. It is emphasized here that \( Z_F \) describes the properties of the electrode which we are actually interested in. In contrast, impedance measurements yield the total impedance \( Z \), i.e. \( Z_F \) concealed by a double layer capacitance \( C_{dl} \). If the origin of \( C_{dl} \) can be attrib-
uted to a space charge at the interface between Pt and YSZ (see e.g. (9)), it can be
assumed that $C_{dl}$ is associated in parallel with $Z_F$. In this case, $Z_F$ and $C_{dl}$ (and
therefore also $R_t$) can be easily obtained from experimentally determined imped-
ance data $Z$, even without any knowledge of the actual electrode mechanism (10).

A SIMPLIFIED MODEL OF THE Pt, O$_2$|YSZ SYSTEM

Model Equations and Assumptions

We consider the electrochemical exchange of oxygen at the Pt,YSZ interface
which is described by the overall reaction

$$\frac{1}{2}O_2 + V_o^- + 2e^- = O_o^x$$  \[9\]

where, in Kröger-Vink notation, $V_o^-$ represents the oxygen vacancies, and $O_o^x$ represents occupied oxygen lattice sites in the YSZ. The overall reaction is consid-
ered to consist of several elementary reactions (cf. Fig. 2): oxygen adsorbs dissoci-
atively (Langmuir-type, no interaction) on the Pt surface, diffuses linearly in the
direction of $z$ perpendicular to the electrode surface, and is electronated and
incorporated into the YSZ near the tpb line (1,2).

Using $[O_{ad}] = N_0\theta$ and $[s] = N_0(1 - \theta)$, where $N_0$ is the maximum
number of adsorption sites and $\theta$ is the fractional coverage, mass and charge bal-
ances (Eq. [1] and Eq. [2]) give:

$$\frac{\partial\theta}{\partial t} = 2k_{ad}P_{O_2}N_0(1 - \theta)^2 - 2k_{des}N_0\theta^2 + k_f(1 - \theta) + \frac{D_d^2\theta}{dz^2}$$  \[10\]

$$g_1: \quad I_F = 2N_0FA\{k_b(1 - \theta) - k_f\theta\}$$  \[11\]

where $k_f = k_f[V_o^-]$, $k_b = k_b[O_o^x]$, and $A$ is the area where the charge transfer reac-
tion takes place. We further assume that $D \neq D(\theta, z)$. The vector of unknown
parameters is given by $p = \{k_1, \alpha_c, k_1, \alpha_a\}_T$, where $T$ simply denotes vector
transposition.

Computer Implementation

Eq. [10] and Eq. [11] represent the non-linear state-space description of the
model (cf. Eq. [1] and [2]). Although explicit solutions for the time and frequency
dependent behaviour are available for this problem (11) (with one-dimensional
boundary conditions at the tpb), we solve these equations numerically since

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explicit solutions are generally not available for equation systems describing higher-order reaction mechanism involving surface diffusion. The finite-difference approach is employed for the treatment of the distributed parameter system. It is assumed that the electronation reaction (R.3 in Fig. 2) is not confined to a one-dimensional line (the tpb line), but that it is extended over a certain width (5 to 50 nm). We further use non-uniform compartment sizes (Fig. 2). Mass and charge balances are written for every compartment, either in algebraic form, or graphically in Simulink, the graphic programming language extension of MATLAB (12). Simulations are run in MATLAB by choosing an appropriate set of parameters and its corresponding starting conditions. Linearized state-space descriptions are obtained either by linearizing the equations algebraically (cf. Eq. [3]) or numerically from the Simulink/MATLAB models. More details will be given elsewhere (7,8).

Structural Properties of the Equations

We obtain a qualitative picture of the frequency response by analysing the transfer function. As a first-order approximation we neglect surface diffusion and write the state-space matrices for the first compartment:

\[
A(p) = \frac{\partial f_1}{\partial x} = -4k_{ad}P_{O_2}N_0(1 - \hat{x}) - 4k_{des}N_0\hat{x} - \hat{k}_f - \hat{k}_b
\]

\[
B(p) = \frac{\partial f_1}{\partial \eta} = 2\alpha_c f\hat{k}_f\hat{x} + 2\alpha_a f\hat{k}_b(1 - \hat{x})
\]

\[
C(p) = \frac{\partial g_1}{\partial x} = 2N_0F A_1(-\hat{k}_b - \hat{k}_f)
\]

\[
D(p) = \frac{\partial g_1}{\partial \eta} = 2N_0F A_1(2\alpha_a f\hat{k}_b(1 - \hat{x}) + 2\alpha_c f\hat{k}_f\hat{x})
\]

where we used \( x = \theta \), the circumflex denotes steady-state values at the operating point, and \( A_1 \) is the area of the first compartment. By using the (physically obvious) constraints \( \alpha_a + \alpha_c - 1 = 0 \) and \( I_F(\eta = 0) = 0 \), the number of independent parameters is reduced by two. The Faradaic impedance is finally obtained as (cf. Eq. [7]):

\[
Z_F(j\omega, p) = R_1\left\{1 - \frac{-\hat{k}_b - \hat{k}_f}{j\omega + 4k_{ad}P_{O_2}N_0(1 - \hat{x}) + 4k_{des}N_0\hat{x}}\right\}
\]
where \( R_t = 1/D \) (cf. Eq. [6]). The expression for \( Z_F(j\omega) \) is a first-order rational fraction in \( j\omega \). It describes a single semi-circle in the fourth quadrant of the complex plane ("capacitive behaviour"). Irrespective of the operating conditions, \( Z_F \) can never show any "inductive behaviour", because the denominator in Eq. [13] can not become negative (at least not for physically plausible parameters) over the entire frequency range. It can be further shown (7) that the system is globally structurally identifiable by electrochemical impedance spectroscopy as well as in the steady state, i.e. there exists one set of parameters which describes the dynamic properties uniquely. In addition, the parameters can be estimated equally well from current–overpotential measurements or from electrochemical impedance measurements.

**Simulations and Discussion**

The kinetic constants, the experimental parameters, and the set of unknown parameters used in the simulations are given as: \( k_{ad} = 1.3 \times 10^5 \, \text{m}^2/(\text{atm}\cdot\text{s}) \); \( k_{des} = 5.7 \times 10^6 \, \text{m}^2/\text{s} \); \( N_0 = 10^{19} \, \text{m}^{-2} \); \( V_o = 4.63 \times 10^3 \, \text{mol}/\text{m}^3 \); \( O^* = 4.45 \times 10^4 \, \text{mol}/\text{m}^3 \); \( D = 8.34 \times 10^{-10} \, \text{m}^2/\text{s} \); \( C_{dl} = 20 \, \mu\text{F} \); \( R_{YSZ} = 0.5 \, \Omega \); \( A_s = 1 \, \text{cm}^2 \); \( L = 10 \, \mu\text{m} \) (thickness of electrode); \( pO_2 = 1 \, \text{atm} \); \( T = 1000 \, \text{K} \); \( \rho_{pb} = 1 \, \mu\text{m}/\mu\text{m}^2 \); \( \Delta s = 10 \, \text{nm} \) (thickness of first compartment; see also Fig. 2); \( k_i^o = 0.24 \, \text{m}^3/(\text{mol}\cdot\text{s}) \); \( \alpha_s = 0.5 \). The magnitude of the kinetic constants is chosen so that the electrode impedance is almost completely charge transfer controlled at zero overpotential. We are aware of the fact that the oxygen reduction at the Pt,YSZ interface is not charge transfer controlled at 1000 K. Some of the rate constants have different magnitudes (8).

The current–overpotential behaviour is given in Fig. 3. Compare this behaviour with the impedance curves (\( Z \) and \( Z_F \)) given in Fig. 4. The fact that the electrode reaction is charge transfer controlled at \( E_{eq} \) is clearly reflected in the impedance and the \( I(\eta) \) curves at low overpotential. The higher the cathodic overpotential (e.g. at \(-0.8 \, \text{V}\)), the more the overall reaction becomes controlled by surface diffusion which is readily seen from the inset in Fig. 4.

Surface diffusion is also rate limiting at low oxygen partial pressures at zero overpotential. Fig. 5 shows the impedance curves for decreasing oxygen partial pressures. With decreasing \( pO_2 \) the charge transfer resistance as well as the concentration impedance increase and the polarization resistance \( R_p \) is increasingly dominated by the concentration polarization term \( R_c \). This fact is summarized in Fig. 6 which shows the various conductivities as a function of \( pO_2 \). From Fig. 5 and Fig. 6 it can be seen that the overall reaction is charge transfer controlled at \( pO_2 > 10^{-2} \, \text{atm} \). At \( pO_2 < 10^{-4} \, \text{atm} \) the electrode resistance is dominated by the adsorption step, whereas surface diffusion is the rate limiting factor at intermediate oxygen partial pressures. These facts are illustrated by the different slopes of the \( \log(1/R_p) \) vs. \( \log(pO_2) \) curve as well as the shape of the complex plane impedance curves.
CONCLUSIONS

We provided a unified framework for dealing with electrode reaction mechanisms in state-space and transfer function form. The structural properties of the model equations can be evaluated from the transfer function. Any input–output behaviour, e.g. current-voltage curves, cyclic voltammetry curves, or impedances, can be simulated from the state-space form under any experimental condition. In a further step, model parameters can be estimated from experimental data.

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Fig. 1. Experimental 4-probe 3-electrode setup for experimental electrode characterization. The working electrode can be considered as a dynamic system whose input-output behaviour is described by its transfer function $Y_F(s)$.

Fig. 2. Assumed first-order reaction mechanism of $O_2$ at the Pt/YSZ interface. The chemical rate constants for adsorption and desorption are taken to be independent on the surface coverage of Pt. The electron transfer is assumed to take place in a single reaction step. The electrochemical rate constants are supposed to be exponentially dependent on the overpotential where $f = F/(RT)$; $\alpha$ are the symmetry coefficients of the electrochemical reaction; $k^+_f$ and $k^-_f$ are the forward and backward chemical rate constants; $n$ is the number of electrons transferred in the reaction step; $T$, $R$, and $F$ have their usual meaning.
Fig. 3. Simulated current-overpotential behaviour at 1000 K using the model Eqs (R1–R3) of Fig. 2. Theoretical Tafel behaviour is also given (straight lines) for the case that the concept of the rate determining step applies to the entire overpotential region. We find by simulation that \( i_{\text{lim}} \approx pO_2^{1/2} \) in the cathodic overpotential range. Note the limiting current behaviour of the cathodic \( I(\eta) \) curve even at \( pO_2 = 1 \text{ atm} \), which is not found experimentally. To improve this particular behaviour, the coverage dependence of \( k_{\text{ad}} \) and \( k_{\text{des}} \) must be taken into account [8].

Fig. 4. Simulated impedance curves for different overpotentials at \( pO_2 = 1 \text{ atm} \) and \( T = 1000 \text{ K} \). Thin curves denote the Faradaic impedance, \( Z_F \), whereas bold curves denote the total impedance, \( Z \), including a double layer capacitance of 20 \( \mu \text{F} \). Compare the impedance curves with the current-overpotential curve at \( pO_2 = 1 \text{ atm} \) (filled circles in Fig. 3). At low overpotentials \( (\eta > 0.2 \text{ V}) \), \( Z \) is charge transfer controlled whereas surface diffusion is rate limiting at high overpotentials \( (\eta < -0.6 \text{ V}) \).
Fig. 5. Simulated impedances for a wide range of oxygen partial pressures. The equilibrium potential $E_{eq}$ is calculated for every $pO_2$ from the condition $I_F(\eta = 0) = 0$, where $E_{eq}$ is set arbitrarily to zero at $pO_2 = 1$ atm. In this way, the electrode potential is defined relative to $E_{eq}$ at 1000 K and $pO_2 = 1$ atm. At $pO_2 \leq 10^{-4}$ atm the impedance is dominated by a low-frequency semi-circle (see inset).

Fig. 6. $pO_2$ dependence of electrode conductivities under zero load. The concentration polarization $R_c$ is defined as the difference between the polarization resistance $R_p$ and the transfer resistance $R_t$. Note that $R_p$ is charge transfer controlled at $pO_2 \geq 10^{-2}$ atm, surface diffusion controlled at $10^{-4}$ atm $< pO_2 < 10^{-2}$ atm, and adsorption controlled at $pO_2 \leq 10^{-4}$ atm. Note also that $R_t$ shows a complicated $pO_2$ dependence.