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# GENERAL FRAMEWORK FOR MATLAB IMPLEMENTATION OF STATE-SPACE MODELING (SSM) APPROACH USED FOR THE INVESTIGATION OF THE REACTION MECHANISMS AT ELECTRODES

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**ABSTRACT**. An approach focusing on the identification of the reaction mechanisms at electrochemical interfaces will be further described. It is based on state-space modeling (SSM) which is an approach used in control theory for the simulation of coupled differential equations. In this case, the state-space modeling approach consists of a combination of modeling, simulations, and experiments.

## 1. INTRODUCTION

The kinetics of the processes at the electrodes go trough is very important for a better understanding and also for an improvement of the performance of electrodes processes. We proposed the steady-space modeling approach for the identification of the reaction mechanisms at electrodes. This is based on the experimental results but also modeling and simulations, using the impedance spectroscopy technique, which is widely used in electrochemistry.

The method is based on transient numerical simulations of the elementary kinetics [1]. Imposing a harmonically varying overpotential leads to a periodic response of the system from which the impedance is obtained.

Impedance measurements used in electrochemistry must be performed at a system in steady state simulation. Normally, impedance measurements are performed under potential control with a steady state current. A small potential disturbance is applied and the current response is measured as it is schematically shown in figure 1. Every system subjected to a perturbation x(t) will determine a response y(t). The system can be described by the following differential equation:

$$a_0 x(t) + a_1 \frac{dx(t)}{dt} + a_2 \frac{d^2x}{dt^2} + \ldots = b_0 y(t) + b_1 \frac{dy(t)}{dt} + a_2 \frac{d^2y}{dt^2} + \ldots \tag{1.1}$$

The impedance is only defined for a linear system i.e. a system with only first order response to the applied potential. However, the current response of a system is not linear as it can be seen in figure 1, which shows a part of the polarization curve. But if the applied disturbance is small the system can be approximated by a linear system.

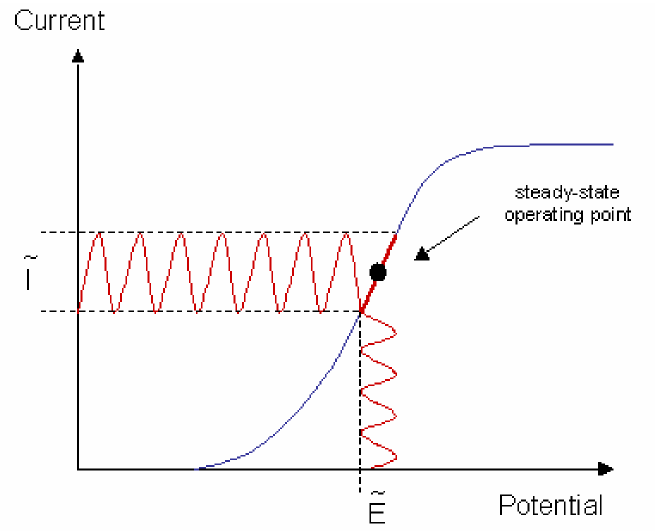

**Figure 1.** The application of a potential disturbance and its current response

The applied disturbance x(t) has a sine wave form: $x(t)=E_m\sin(\omega t)$ and the response $y(t)=I_m\sin(\omega t+\Phi)$, where *t* is the time, $E_m$ and $I_m$ the amplitudes, ω the angular frequency, Φ the phase difference between the voltage and the current.

The impedance, Z is then defined as:

$$Z(\omega)=\frac{\Delta E(\omega,t)}{\Delta j(\omega,t)}=\frac{E_m}{I_m}\cdot e^{i\Phi} \tag{1.2}$$

Using the Euler relation:

$$e^{i\Phi}=\cos\Phi+i\sin\Phi \tag{1.3}$$

the impedance becomes:

$$Z(\omega)=Z'(\omega)+iZ''(\omega) \tag{1.4}$$

where:

$$Z'(\omega)=\text{real}(Z)=|Z|\cos\Phi \tag{1.5}$$

$$Z''(\omega)=\text{imag}(Z)=|Z|\sin\Phi \tag{1.6}$$

$$|Z|=\frac{E_m}{I_m}=\sqrt{Z'+Z''} \tag{1.7}$$

$$\tan\Phi=\frac{Z''(\omega)}{Z'(\omega)} \tag{1.8}$$

The method represents a numerical experiment of impedance measurements using frequency response analysers. It allows the calculation of impedance spectra based on elementary electrochemistry without the necessity of applying equivalent circuit models [2,3]. By fitting simulated spectra to experimental data, kinetic parameters (exchange current density, reaction rate constant) are obtained directly.

## 2. CHARACTERISTIC PARAMETERS

Impedance spectra can be plotted in two ways: in the Nyquist representation where the negative imaginary part of the impedance, Z'', is plotted vs. the real part of the impedance, Z' (Fig.3) or in the Bode representation where the absolute impedance, |Z|, as well as the phase shift, Φ, are plotted vs. the angular frequency ω (Fig.2).

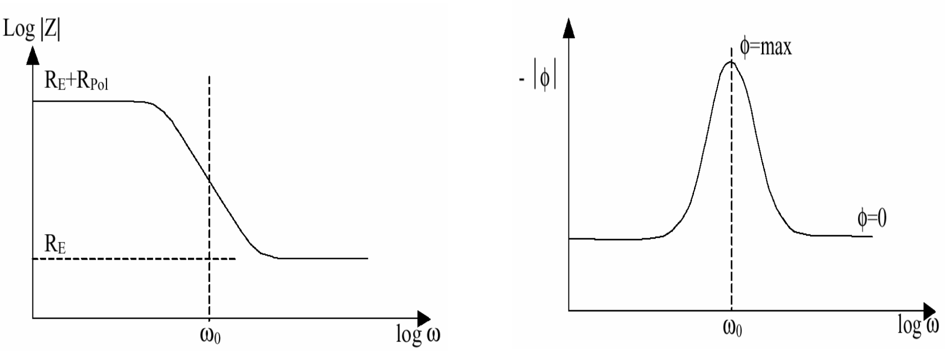

**Figure 2**: Bode plot

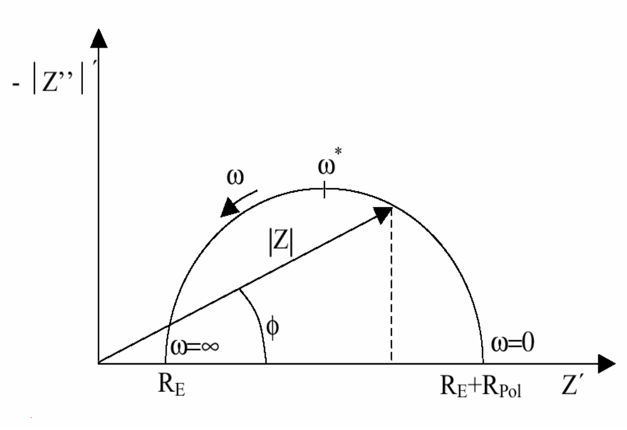

**Figure 3.** Nyquist plot

Both representations contain, in principle, the same information and can be transformed into each other. However, depending on the data, one or the other representation is preferred because specific details can be resolved more precisely. Hence, in impedance analyses, both representations must always be considered. The following characteristic parameters are obtained from the impedance data:

- the *polarization resistanc*e, $R_{pol}$, which is the purely ohmic part of the electrode resistance. It can be determined from both Nyquist as well as from Bode plot (Fig.2, Fig.3)

- the *electrolyte resistanc*e, $R_e$, which is caused by a certain contribution of the electrolyte. It can be determined from the high frequency part of Nyquist plot at the intersection of the impedance data with the real axis (Fig. 3).

- th*e relaxation frequenc*y, ω*, which is defined as the frequency at the maximum imaginary impedance value. In the case of several relaxation processes, there are several relaxation frequencies, which can be identified as local maxima in the Nyquist plot [4,5,6]

## 3. MODELING

There are two different models possible for interpreting EIS measurements:

a. electrical equivalent circuit models - interpretation of the electrical models in terms of the fundamental physical or chemical parameters is often difficult [7,8]

b. elementary kinetic models - represents a more fundamental description of the involved physicochemical processes

For the identification of the reaction mechanisms at electrodes was used the state-space modeling approach that is based on a combination of experiments, modelling and simulations.

Data from surface science literature were used for the prediction of the main reaction steps that might take place at the electrochemically active interface. The electrochemical model consists of a set of possible chemical and electrochemical reactions that are derived from the relevant surface science literature.

The chemical and the electrochemical equations of the model can be formulated as mass and charge balances.

The kinetic constants of the chemical and electrochemical reactions will first be estimated for our particular model with the help of literature data and afterwards by an optimization procedure using an electrochemical impedance measurement under well-defined operating conditions.

The state-space model is believed to be the most reliable linear time-dependent model to use for computer analysis [9,10]. The general state-space representation is: $\dot{x}(t,p) = \frac{dx(t,p)}{dt} = f[x(t,p),u(t),t,p]$ where x(t,p) represents the vector of the state-variables depending on the time t, and the vector of unknown parameters, p. The vector u(t) signifies the input variables that can be varied in the experiments and in the simulations.

In addition to the differential equations, the state-space description contains the observation function y(t,p), which denotes the observed quantities and is referred to as the model output. $y(t,p) = g[x(t,p),p]$

The variables in the general state-space model can be directly interpreted in terms of the kinetic variables used in the electrochemical model. The vector of state-variables, x(t,p), represents the surface concentrations of the different adsorbed species. The concentration of the adsorbed species is a function of the time, t, and the vector of unknown parameters, p, i.e. the reaction rate constants and the surface coverage values. The vector u(t) signifies the overpotential, η ,and the model output, y(t,p), can be interpreted as the Faraday current, $I_F$ .

The simulation algorithm is the following: in a first step, the electrochemical model is linearized. Afterwards, a Laplace transformation is used in order to transfer the system into the frequency domain. Third step-the impedance is calculated.

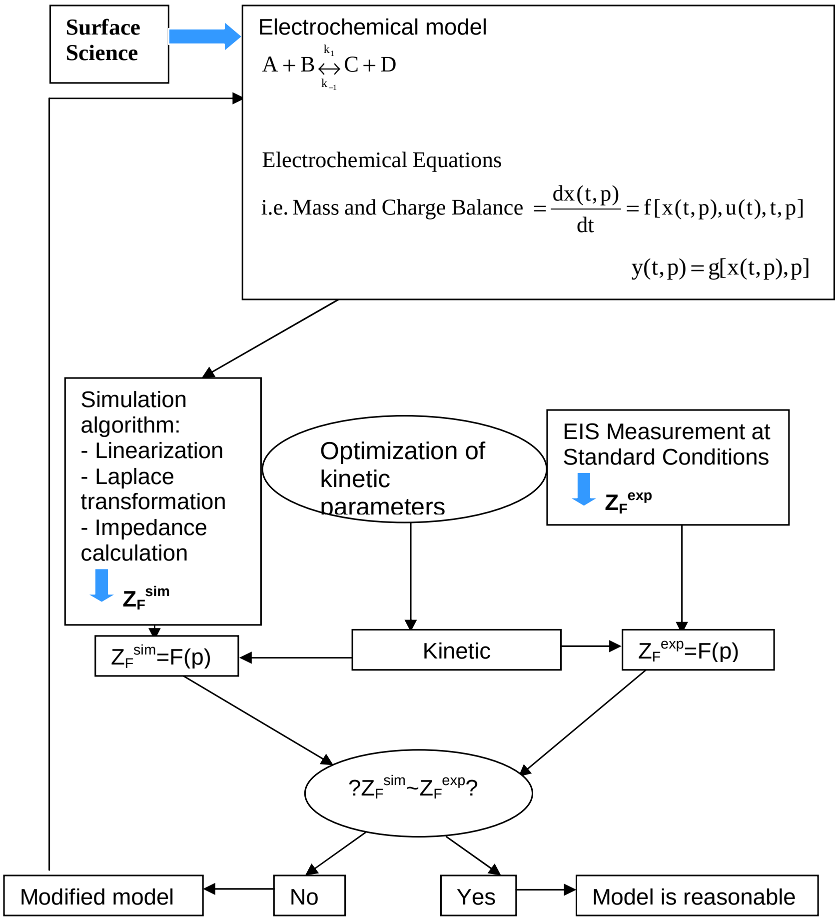

**Figure 4.** State-Space Modeling (SSM) approach for the investigation of the reaction mechanisms at electrodes

An electrochemical impedance spectrum will then be simulated directly from the electrochemical model [11]. The model spectrum as well as simulations under varying parameters will be compared to experimental data under the same conditions in order to prove the validity of the chosen model.

The electrochemical model consists of a set of possible chemical and electrochemical reactions that are derived from the relevant surface science literature. These reactions are of the following form:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C + D \tag{3.1}$$

where *A*, *B*, *C*, and *D* are gas phase species, surface species, adsorption sites, or electrons; $k_1$ and $k_{-1}$ are the reaction rate constants for the forward and the backward reaction, respectively. In order to establish an electrochemical model, which describes the entire system, several assumptions have to be taken into consideration.

For instance, the number and the kind of surface species, their diffusion and their reaction behavior have to be estimated. As many of the kinetic constants are not known from the literature, it is necessary to estimate the unknown kinetic constants.

The chemical and the electrochemical equations of the electrochemical model can be formulated as mass and charge balance.

The mass balance concerning the time-dependent surface species *C* in eq. 3.1 is given as:

$$[\dot{C}] = \frac{d[C]}{dt} = k_1[A][B] - k_{-1}[C][D] \tag{3.2}$$

In the case of several parallel and consecutive reactions as well as several surface species, a whole system of coupled differential equations results. The system becomes very complex and cannot be solved analytically anymore. For a numerical solution, the electrochemical model must be written in a form that can be used for computer analysis.

## 4. SIMULATIONS

Having established an electrochemical model for the system, it is now required to implement the system into the computer. An impedance spectrum, $Z_{F\ sim}$, can then be simulated and can be compared to the experimental EIS data, $Z_{F\ exp}$. The simulations are carried out using the computer program MATLAB® with the graphical programming extension SIMULINK that is used in control theory for simulations of dynamic systems [12,13,14,15].

SIMULINK is designed as a unit construction system. The mathematical equations are built from construction blocks given in the program. An illustrative example is shown in Fig. 5. There the computer implementation for the calculation of the surface concentration *C* according to Eq. 3.2 is illustrated. The concentrations *A*, *B*, and *D* are assumed to be constant and are illustrated as boxes in Fig. 5. The triangles containing $k_1$ and $k_{-1}$ represent multiplications, whereas the program element 1/s stands for the integration of a Laplace transformed variable.

The output is shown in the display box and represents, in this example, the concentration of the surface species *C*.

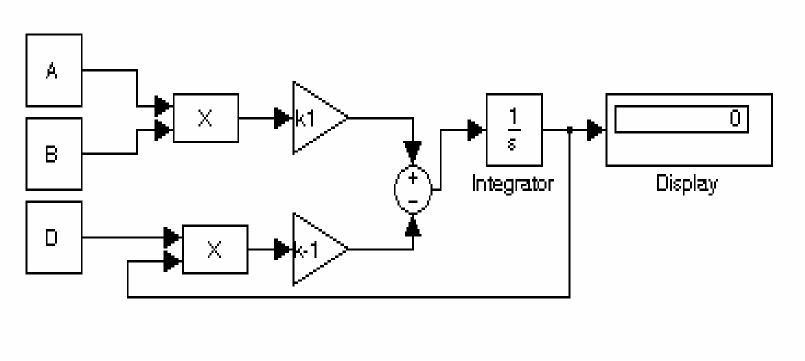

**Figure 5.** Simulink block diagram

## 5. CONCLUSIONS

The concept of the present study was presented by investigating the reaction mechanism.

An electrochemical impedance spectrum will then be simulated directly from the electrochemical model. The model spectrum as well as simulations under varying parameters will be compared to experimental data under the same conditions in order to prove the validity of the chosen model.

Steady-space modeling approach and implementation of this in Matlab that we proposed, make easier the work of solving a set of equations, permits determination of the kinetic parameters and could give us a explanation of the chemical processes that are happening to the electrode. The electrical equivalent circuit models for a complex process could not do this explanation so why this approach is recommended.

State-space models can accommodate any degree of complexity, the need for testing the structural proprieties demands rather than simple equations. A case study using SSM approach will be presented in the next article as application at this general framework paper.

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