REACTION PATHWAYS AND KINETICS OF OXYGEN REDUCTION AT LSM CATHODES

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ABSTRACT

The mechanism and kinetics of oxygen reduction at the La$_{0.85}$Sr$_{0.15}$MnO$_3$/YSZ interface is investigated with electrochemical impedance spectroscopy and State-Space Modelling. This simulation approach allows for the calculation of the faradaic impedance directly from a reaction model without using any equivalent circuits, whose physical interpretation is ambiguous in terms of reaction mechanism and kinetics. A simple reaction model accounting for dissociative oxygen adsorption and charge transfer is proposed. The comparison of simulated and experimental impedance data shows that the proposed model describes the oxygen reduction reaction fairly well. The reaction kinetics exhibits a mixed control by oxygen adsorption and charge transfer.

INTRODUCTION

The identification of reaction mechanisms and kinetics taking place at solid oxide fuel cells (SOFC) electrodes is of great interest. Clarifying what limits the electrochemical processes helps to tailor the electrodes of the SOFC in order to improve its overall performances. Oxygen reduction takes place at the cathodic side of SOFC, as well as a significant fraction of the cell losses. Although oxygen reduction reaction has been extensively studied (1,2 and references therein, 3-6), it is not clearly understood how the reaction proceeds in detail. A widespread technique to investigate this reaction is Electrochemical Impedance Spectroscopy (EIS). Usually impedance data are fitted with electrical equivalent circuits. However their interpretation in terms of reaction mechanisms and kinetics turns out to be difficult and ambiguous which limits drastically the comprehension of the processes. A recently developed approach, State-Space Modelling, consists in simulating the faradaic impedance directly from a reaction model without using electrical equivalent circuits. The present work focuses on the application of State-Space Modelling to the investigation of oxygen reduction at a La$_{0.85}$Sr$_{0.15}$MnO$_3$/YSZ interface.

STATE-SPACE MODELLING (SSM)

State-Space Modelling (5, 6) enables to calculate the impedance of electrochemical reactions. This approach is based on the calculation of a transfer function derived from a
reaction model that accounts for mass transport and charge transfer. The resulting system of equations is called state-space model and can be written as follows:

\[
\begin{align*}
\dot{\theta}(t,p) &= f[\theta(t), \eta(t), p] \\
I_F(t,p) &= g[\theta(t), \eta(t), p]
\end{align*}
\]

\[1\]

\[2\]

\(\theta\) is the state variable and represents the state of the system under given operating conditions (overpotential, temperature, oxygen partial pressure...). \(\eta(t)\) is the overpotential of the cathode, \(I_F\) the faradaic current, \(t\) is the time and \(p\) the vector of the rate constants of the reaction model.

State-Space Modelling is carried out under steady-state conditions. The state-space model is linearized and undergoes a Laplace transform. This results in a direct relationship between the overpotential and the current (eq. \[3\]).

\[I_F(j\omega,p) = Y_F(j\omega,p) \eta(j\omega)\]

\[3\]

The complex transfer function \(Y_F(j\omega,p)\) is the admittance. The faradaic impedance \(Z_F(j\omega,p)\) is obtained by taking the reciprocal of \(Y_F(j\omega,p)\). \(Y_F(j\omega,p)\) and \(Z_F(j\omega,p)\) depend on the angular frequency \(\omega\) and on the vector \(p\). It appears clearly that it is possible to calculate the faradaic impedance directly from a reaction model when \(p\) and \(\omega\) are known.

MODEL AND SIMULATIONS

In this study we only consider the case of electronic conducting cathode. In this case the standard cathodic interface is LSM/YSZ at low overpotential \(\eta\). A first reaction model for oxygen reduction is studied. It simply consists in a dissociative oxygen adsorption at the cathode surface followed by a charge transfer at the triple phase boundary. Surface diffusion of adsorbed oxygen is considered as infinitely fast and is not taken into account in this first model.

\[
\begin{align*}
K_A & \quad \text{O}_2 \leftrightarrow 2 \text{O}_{AD} \\
K_D & \quad \text{O}_{AD} + 2e^- \leftrightarrow \text{O}_O
\end{align*}
\]

\[4\]

\[5\]

with \(K_A\) and \(K_D\) respectively denoting the rate constants of adsorption and desorption, and \(K_F\) and \(K_B\) the forward (reduction) and backward (oxidation) electrochemical reaction. Note that \(K_F\) and \(K_B\) depend on the cathode overpotential \(\eta\).
For this model, the state-space variable, $\theta_{ad}$, is the cathode surface coverage of adsorbed oxygen $O_{ad}$ and $p = [K_A, K_D, K_F(\eta), K_B(\eta)]$. Figure 1 shows the SSM calculation of impedance corresponding to the proposed reaction mechanism. It is found that the simulated impedance spectrum can always be plotted with a simple electrical equivalent circuit, whatever the values of the rate constants are.

![Diagram](image_url)

**Fig.1**: Simulated Nyquist plot of the reaction model (reactions [4] and [5]) and corresponding equivalent circuit.

Unlike the standard equivalent circuit approach, State-Space Modelling allows to relate directly $R_1$, $R_2$ and $C$ to the rate constants of the reaction. As an example, the following relationships can be established when $K_A$ equals $K_D$:

$$R_1 \propto \frac{2K_A + K_F + K_B}{K_A(K_F + K_B) + 2K_F K_B}$$ [6]

$$R_2 \propto \frac{K_F + K_B}{K_A}$$ [7]

$$C \propto \frac{K_A(K_F + K_B) + 2K_F}{(K_F + K_B)(2K_A + K_F + K_B)}$$ [8]

One can clearly see that $R_1$, $R_2$ and $C$ are dependant on all the rate constants $K_A$, $K_F$ and $K_B$. Consequently it is *a priori* not possible to assign one elementary reaction step to $R_1$ or to the semi circle ($R_2$-$C$) as it is usually done with an experimental equivalent circuit approach (equivalent circuits derived directly from the experimental impedance). Stress is also laid on the fact that the capacitance $C$ originates from the reaction kinetics and must not be mixed up with a double layer capacitance.

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In order to compare simulated and experimental impedance data, the resistance of the electrolyte, $R_{EL}$, and the double layer capacitance, $C_{DL}$, has to be taken into account. The total impedance $Z_{SIM}$ can be defined as outlined in Figure 2. Note that $C_{DL}$ is a pure capacitance or a constant phase element (CPE). As $C_{DL}$ and $C$ are parallel, great care has to be taken as regards the capacitive behavior of $Z_{SIM}$. This behavior can be attributed to the faradaic capacitance $C$ or to the electrical double layer $C_{DL}$ (or both). This notably affects the value of $Z_{SIM}$ at high frequency, as schematically illustrated in figure 3.

![Diagram](image)

**Fig.2:** The total impedance $Z_{SIM}$ is composed of the faradaic $Z_f$, the double layer capacitance $C_{DL}$ and the resistance of the electrolyte $R_{EL}$.

![Diagram](image)

**Fig. 3:** Schematic representation (Nyquist plots) of $Z_{SIM}$, depending of the value of $C_{DL}$ and $C$. $f$ denotes the frequency. When the faradaic capacitance $C$ is much greater than the double layer $C_{DL}$ (a), the intercept of the impedance on the real axis at high frequency $R_{HF}$ is dependant on the reaction kinetics ($R_{EL} + R_1$).

A numerical optimization process allows for the comparison of simulated ($Z_{SIM}$) and experimental ($Z_{EXP}$) impedance data. The rate constants and eventually $C_{DL}$ are used as variables to minimize the difference $|Z_{SIM} - Z_{EXP}|$. Simulations and numerical optimization
are performed with a Matlab®5.2/Simulink®2.2 software package (The Mathworks Inc., USA)

EXPERIMENTAL

The cell (3 electrodes) used for EIS measurements is built up as follows: the LSM (La0.85Sr0.15MnO3) paste is prepared by mixing the perovskite starting powder (69 wt%) (SSC Inc., USA) with a solvent, diethylene glycol monobutyl ether acetate (24.8 wt%) (Fluka, Switzerland), a dispersant, furan-2-carboxylic (0.9 wt%) (Fluka, Switzerland) and a binder, ethyl cellulose (5.3 wt%) (Fluka, Switzerland) in an agate mortar. The working electrode (cathode) and the reference electrode are made by screen-printing this paste (325 mesh, 15μm thick) onto a 150 μm thick YSZ electrolyte (8 mol% Y2O3) (Kerafol, Germany). The half-cell is sintered in air at 1000°C during two hours. The cathode has a homogeneous and porous microstructure and adheres well to the electrolyte. It exhibits a conductivity of around 100 S.cm⁻¹ at 800°C in air.

EIS measurements are performed potentiostatically with a Zahner IM-6 Impedance Measurement Unit (Zahner Messtechnik, Germany) at 800°C. The frequency range is 1Hz-300KHz. The sinusoidal voltage perturbation has an amplitude of 10 mV.

SELECTED RESULTS

Qualitative analysis

The impedance of the LSM/YSZ cathodic interface has been measured as a function of its overpotential (figure 4) and of the oxygen partial pressure pO₂ (figure 5). It appears that the impedance decreases with more negative potentials and higher pressures. The intercept of impedance arc with the real axis at high frequency (Rhf) is almost constant with respect to oxygen partial pressure and overpotential changes. If Rhf corresponded to the ohmic contribution of the faradaic impedance (Rf), Rhf would significantly change when η and pO₂ are varied, which is not the case. Therefore Rhf is associated to a constant resistance of the electrolyte (Rhf ~ Res).

The impedance spectra exhibit one depressed semi-circle, except at low oxygen partial pressures where two depressed semi-circles evolve. Since Rhf ~ Res, the depressed semi-circle shape of ZEXP is related to the electrical double layer (and not to the faradaic capacitance C) which is represented as a constant phase element (CPE), often used to describe charge distribution at heterogeneous interfaces. This constant phase element obscures the faradaic impedance, which make the qualitative interpretation of the impedance spectra difficult.
Fig. 4: Experimental impedance, $Z_{\text{EXP}}$, as a function of the cathode overpotential $\eta$. The numbers inside the graph denote the frequency of the solid points.

Fig. 5: Experimental impedance, $Z_{\text{EXP}}$, as a function of the oxygen partial pressure $p_{O_2}$. The numbers inside the graph denote the frequency of the solid points.

**Quantitative analysis**

A numerical optimization between simulated and experimental impedance enables the estimation of the CPE contribution and the calculation of the reaction kinetics parameters.
In the present reaction model, $K_i(\eta)$ and $K_B(\eta)$ are expressed as:

$$K_i(\eta) = k_F e^{-\beta F\eta/RT} \quad [6]$$
$$K_B(\eta) = k_B e^{(1-\beta)F\eta/RT} \quad [7]$$

where the pre-exponential terms $k_F$ and $k_B$ are independent of the overpotential $\eta$, $n$ is the number of exchanged electrons ($n = 2$), $\beta$ the transfer coefficient ($\beta = 0.5$), $F$ the Faraday constant, $R$ the gas constant and $T$ the temperature ($T = 800^\circ C$).

The constant phase element is defined as $1/Z_{CPE} = C_{DL} (j\omega)\phi$, with $\phi \sim 0.7$. $C_{DL}$, $K_A$, $K_D$, $k_F$ are independent parameters to be varied following a home-made optimization process in order to minimize the difference between simulated and impedance data. The choice of the reference electrode makes $k_S$ dependent on $K_A$, $K_D$ and $k_F$. Therefore $k_B$ is not used in the optimization process.

Only the experimental data of Fig. 4 ($Z_{\text{EXP}}$ as a function of $\eta$) have been used to carry out the numerical optimization. At the time when the present paper is written, an optimization program using simultaneously both kind of experimental data ($Z_{\text{EXP}}$ as a function of $\eta$ and of $pO_2$) is under development. The results of the numerical optimization are shown in figure 6 and 7. The rate constants (and the double layer capacitance) are inserted in the graphs. They account for a mixed control by adsorption and charge transfer.

![Graph](image.png)

**Fig. 6:** $Z_{\text{EXP}}$ and $Z_{\text{SIM}}$ at 800°C in air at -50 mV after numerical optimization. The numbers inside the graph denote the frequency of the solid points.

The values $R_1$, $R_2$ and $C$ of the faraday impedance are presented in table 1. They are directly calculated from the obtained kinetics parameters. As expected, the faradaic impedance $C$ is much smaller than the double layer capacitance $C_{DL}$. Both $R_1$ and $R_2$ vary...
with the overpotential, which confirms that it is not possible to assign one resistance or one impedance arc to any unique reaction step.

\[
\begin{align*}
K_A &= 3 \times 10^5 \text{ s}^{-1} \\
K_D &= 3 \times 10^5 \text{ s}^{-1} \\
k_F &= 10^6 \text{ s}^{-1} \\
C_{DL} &= 350 \mu\text{F}
\end{align*}
\]

Fig. 7: Simulated impedance \( Z_{\text{SIM}} \) at 800°C in air after numerical optimization as a function of the overpotential \( T \). The numbers inside the graph denote the frequency of the solid points. This figure has to be compared with figure 4.

Figure 6 shows the comparison between experimental and simulated data. For sake of clarity, the plots for one overpotential only (-40mV) are presented. An acceptable agreement between both spectra is found. This is also the case for the other overpotentials. One may object that a better "fit" could be found by drawing equivalent circuits directly from the experimental data. However, the interpretation of such equivalent circuits is very ambiguous and allows neither for the identification of the reaction steps nor for the assessment of kinetics. With State-Space Modelling, the goal is to find a set of reaction parameter which can comprehensively describe the experimental impedance when the overpotential and oxygen partial pressure are varied, as illustrated in figure 7.

| Table 1. Values of the \( Z_f \) equivalent circuit after numerical optimization. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| \( R_1 (\Omega) \) | 0 mV | -40 mV | -75 mV | -110 mV |
| 6.16 | 4.26 | 3.24 | 2.68 |
| \( R_2 (\Omega) \) | 1.95 | 1.47 | 1.38 | 1.52 |
| \( C (\mu\text{F}) \) | 0.8 | 1.1 | 1.1 | 1.0 |

The kinetics parameters obtained from the numerical optimization allows the suggested reaction model to describe \( Z_{\text{EXP}} \) fairly well when the overpotential is varied. Yet those results has to be considered as "provisional" since the experimental data related to the change of oxygen partial pressure has still to be implemented in the optimization process.
CONCLUSIONS

The present study demonstrates that State-Space Modelling is a meaningful approach to interpret impedance spectra and identify reaction mechanisms and kinetics. A first simple mechanism has been proposed for oxygen reduction at an electronic conducting SOFC cathode. Owing to a combination of simulations, experiments and numerical optimization, it was possible to separate faradaic and non-faradaic impedance. However, the present model still has to be tested with respect to variations of oxygen partial pressure. Furthermore it is needed to test other reaction models and notably models including surface diffusion of oxygen. These upcoming advances will be presented at the conference.

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