THE OXYGEN REDUCTION KINETICS OF MIXED CONDUCTING ELECTRODES: MODEL CONSIDERATIONS AND EXPERIMENTS ON La$_{0.6}$Sr$_{0.4}$Co$_{0.8}$Fe$_{0.2}$O$_3$ MICROELECTRODES

J. Fleig, F. S. Baumann, and J. Maier
Max-Planck-Institute for Solid State Research
Heisenbergstraße 1, 70569 Stuttgart, Germany

ABSTRACT

A model is presented that yields current–voltage relations for electron transfer reactions at the electrode/gas interface of mixed conducting electrodes. The approach introduced appears necessary since the relevant electrostatic potential step at the gas/solid interface is not equivalent to the applied overpotential. As a consequence, surprising features such as an additional factor of two in the exponents of the current-voltage (I-V) relation or limiting currents even if charge transfer is the rate determining step are deduced depending on adsorption site concentration, type and equilibrium concentration of adsorbed surface species, etc. Experiments with well-defined La$_{0.6}$Sr$_{0.4}$Co$_{0.8}$Fe$_{0.2}$O$_3$ microelectrodes on yttria-stabilized zirconia electrolytes were performed to investigate the mechanism of the oxygen reduction reaction. A comparison of the measured I-V characteristics with the model calculations suggests that the electron charge transfer to an adsorbed O$_{ad}$ atom is the rate limiting step of the corresponding reduction reaction. Further measurements, however, are required to verify this conclusion.

INTRODUCTION

The slow kinetics of the oxygen reduction taking place at cathodes of solid oxide fuel cells (SOFCs) is one of the major problems to overcome when aiming at lower cell operation temperatures. Despite this, the mechanism of the corresponding electrochemical reaction ($O_2 + 4e \rightarrow 2O^2-$) is still not well understood. This may partly be related to the fact that experiments are rarely performed at well-defined, simple electrodes and thus are often difficult to interpret. Quantitative models to analyze electrochemical experiments, on the other hand, are also only partly established (1-4) and formulas derived for electrochemical reactions at electrode/electrolyte interfaces are often applied to electrode/gas interfaces without critically discussing their validity.

In this presentation it is firstly shown how current-voltage (I-V) relationships can be deduced for rate limiting electron transfer reactions at the surface of mixed conducting SOFC electrodes. The well-known relation $I = I_0[\exp(\beta_a V/RT) - \exp(-\beta_c V/RT)]$ turns out to fail in describing the corresponding charge transfer kinetics. In the second part, experiments conducted on geometrically and structurally well-defined...
La$_{0.6}$Sr$_{0.4}$Co$_{0.8}$Fe$_{0.2}$O$_{3-8}$ microelectrodes on yttria-stabilized zirconia electrolytes are presented and discussed in terms of the reaction mechanism.

**ELECTRON TRANSFER AT GAS/SOLID INTERFACES OF MIXED CONDUCTING ELECTRODES**

In many cases electron and ion transfer reactions at electrode/electrolyte interfaces lead to current-voltage relations of the form

$$j = j^0 \left( \exp \left( \frac{\beta_e F \eta}{RT} \right) - \exp \left( -\frac{\beta_e F \eta}{RT} \right) \right)^{[1]}$$

(5-10) with current density $j$, exchange current density $j^0$ and $F$, $R$, $T$, $\beta_e$ denoting Faraday's constant, gas constant, temperature and transfer coefficients, respectively. The overpotential $\eta$ is the deviation of the electrostatic (Galvani) potential step across the electrode/electrolyte interface $\varphi_{\text{ode}} - \varphi_{\text{ele}}$ (Fig. 1) from its equilibrium value. One might be tempted to use Eq. [1] to also quantify the I-V characteristics of charge transfer reactions taking place at gas/solid interfaces of mixed conducting electrodes (see Fig. 1). However, owing to two problems this is not a reasonable approach:

![Figure 1. Model reaction mechanism used to derive the current voltage characteristics of an electron transfer step at a electrode/gas interface.](image)

i) At the surface of a mixed conducting electrode there is an electrostatic surface potential step $\chi = \varphi_{\text{ode}} - \varphi_{\text{ad}}$, cf. Fig. 1. If an overpotential is applied to the electrode, the surface potential step is modified by $\Delta \chi$ from its equilibrium value $\chi^{eq}$ according to

$$\Delta \chi = \chi - \chi^{eq} = \varphi_{\text{ode}} - \varphi_{\text{ad}} - \left( \varphi_{\text{ode}}^{eq} - \varphi_{\text{ad}}^{eq} \right). \quad [2]$$

This $\Delta \chi$ leads to modifications of the backward and forward reaction rates and thus contributes to a net reaction, i.e. a current. However, in general the overpotential $\eta$ present at the electrode/electrolyte interface and the change of the potential step at the surface, $\Delta \chi$, are different. A basic assumption in the derivation of Eq. [1], namely that the
electrostatic potential step at the relevant interface changes by \( \eta \) upon current, is therefore not valid.

ii) When deriving Eq. [1] it is assumed that, due to a "supporting" electrolyte, the concentration of the species involved in the charge transfer reaction does not have to change upon bias. At electrode/gas interfaces, on the other hand, a double layer is realized by adsorbed ions and in an atmosphere containing oxygen and an inert gas (e.g. \( N_2 \)), these are most probably ionic oxygen species only. Consequently, electrochemically inactive ("supporting") ionic surface species that could establish \( \chi \) are not available. Hence, any potential step change \( \Delta \chi \) is inherently coupled to a change of the concentration of the electrochemically relevant oxygen ad-ions.

In order to derive an appropriate relation for electron transfer as rate limiting step at gas/solid interfaces we consider the model reaction sketched in Fig. 1: Oxygen adsorbs as a molecule on the mixed conductor surface and dissociates into ad-atoms \( O_{ad} \). Both steps are assumed to be fast. An electron transfer leads to \( O^2_{ad} \) and this ad-ion is then incorporated into an oxygen vacancy of the mixed conductor where it receives another electron to become \( O^2 \). This last ionization and the ion incorporation are also considered to be fast. Likewise, the transport of \( O^2 \) through the mixed conducting electrode and its charge transfer into the electrolyte are fast. Hence, the electron transfer \( O_{ad} + e^- \rightarrow O^2_{ad} \) is rate limiting.

In Ref. (4) it is detailed that using a conventional kinetic ansatz the relation

\[
j = \frac{k^{eq} \theta^{eq}}{\theta^{eq}_{O_{ad}}} \exp \left( \frac{\alpha F \Delta \chi}{RT} \right) - \exp \left( -\frac{(1-\alpha) F \Delta \chi}{RT} \right)
\]

results with \( k^{eq}, \theta \) indicating the reaction rate constant of the oxidation reaction and a surface coverage, respectively. The relevant surface potential step \( \Delta \chi \), and the surface coverage of the ionized species have to be expressed in terms of the measurable overpotential \( \eta \) to obtain a usable I-V relation. In Ref. (4) this relation is derived. Essentially two additional equations have to be considered: i) the equilibrium condition of the reactions following the rate limiting charge transfer, i.e. \( O_{ad} + e^- \rightarrow O^2_{electrolyte} \) and ii) the solution of Poisson's equation relating electrostatic potential and concentrations, i.e. \( \theta_{O_{ad}} = \theta^{eq}_{O_{ad}} + \Delta \chi / \chi_{max} \) with \( \chi_{max} \) denoting the surface potential step if all surface sites were occupied by \( O_{ad} \). A system of equations results that can be solved only numerically. Fig. 2 displays some numerically calculated I-V curves for different parameters \( \chi_{max} \) and \( \theta^{eq}_{O_{ad}} \); Tafel-like behavior (straight lines in the log plot) can be found as well as curves strongly differing from a simple Tafel line. Even anodic and cathodic limiting currents may result.

However, we identified two limiting situations for which analytical I-V formulas can be found (4): This is the case if the surface has either a high number of surface sites and a moderate equilibrium surface coverage \( \theta^{eq}_{O_{ad}} \) ("buffered" surface) or only very few ionized
surface species ("unbuffered" surface). These two cases are quantified in more detail in Ref. (4).

\[ j = j^0 \left( \frac{2\alpha F\eta}{RT} - \exp \left( -\frac{2(1-\alpha) F\eta}{RT} \right) \right) \quad [4] \]

\[ j = j^0 \left( \frac{1}{(1-\theta_{eq} \sigma_{eq}) \cdot \exp \left( -\frac{2F\eta}{RT} \right) + \theta_{eq} \sigma_{eq}} \right) - 1 \quad [5] \]

is found. In this case we find limiting currents at anodic as well as cathodic voltages. It should be emphasized that this is not due to conventional concentration polarization since all preceding and subsequent electrochemical, chemical and mass transport steps are

Figure 2. Calculated current voltage curves for different maximum surface potential steps \( \chi_{max} \) and surface coverage of \( O_{ad} \) (\( \theta_{eq} \)) indicating that Tafel behavior is often not observed even though electron transfer is the rate limiting step.
assumed to be fast. It is truly a quality of the electron transfer process at the mixed conductor surface and due to the fact that in "unbuffered" situations the surface potential step $\chi$ is almost independent of the overpotential (cf. Fig. 3) and changes of the (small) concentrations of adsorbed species at the surface drive the current. Accordingly, the charge transfer coefficient $\alpha$ does no longer appear in the I-V relation. Further information and also limitations of this model are discussed in Ref. (4).

Figure 3. Relation between surface potential change $\Delta \chi$ and applied overpotential for different parameters ($\chi_{\text{max}}$, surface coverage of $O_{\text{ad}}$ ($\Theta_{\text{ad}}$)). The diagram shows that the change of the surface potential step can be twice as large as the overpotential (buffered systems) or almost overpotential-independent (unbuffered systems).

**EXPERIMENTS WITH MIXED CONDUCTING MODEL ELECTRODES**

In order to get reliable experimental data on the kinetics of the oxygen reduction reaction it is advantageous to use well-defined, simple model electrodes. Therefore, dense $La_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ (LSCFO) microelectrodes were prepared in the following way: First a thin film of LSCFO was deposited on a 5 mm x 5mm x 0.5 mm polished YSZ (9.5 mol% yttria doped ZrO$_2$) single crystal (CrysTec GmbH, Germany) with (100)-orientation by the PLD (Pulsed Laser Deposition) technique at a substrate temperature of 800°C and p(O$_2$) = 0.4 mbar. From that film, circular microelectrodes of nominal diameters between 20 $\mu$m and 100 $\mu$m were prepared by photolithography. A photograph of the resulting microelectrodes is shown in Fig. 4.

Before microstructuring, the films were characterized by X-ray diffraction (Philips, PW 3710/3020). Additional films were measured after treatments at different temperatures and times of annealing to test their chemical stability. The prepared film shows only few X-ray diffraction peaks, which can be related to the compound $La_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$. The strongest signals were detected at $2\theta = 33.1^\circ$ and $69.5^\circ$, which can be identified with
the (110) or (104) orientation. Another signal which is more than 3 orders of magnitude weaker is visible at 47.5°. This can either be the (012)-orientation of LSCFO or the (440)-peak of a possible reaction product between YSZ and LSCFO, i.e., La$_2$Zr$_2$O$_7$. In the literature, La$_2$Zr$_2$O$_7$ formation at YSZ/LSCO interfaces at high temperatures has often been reported (11-13). However, there is some disagreement about the minimum temperature required for this reaction. Therefore, we annealed a film at 750°C, 800°C and 850°C and measured an XRD-diffractionogram after each step. After 35 hours at 750°C, a slight increase of the signal at 47.5° and the occurrence of two very small new reflections at 21.7° and 44.4° were observed. These new peaks can, together with two other peaks which become visible after 10 h at 850°C, unambiguously be assigned to the reaction product SrZrO$_3$. All these peaks are broad, as often observed for reaction products at solid-solid interfaces. To summarize, the La$_{0.6}$Sr$_{0.4}$Co$_{0.8}$Fe$_{0.2}$O$_{3.8}$ film was grown highly textured (if not epitaxially) on the YSZ substrate. At high temperatures, SrZrO$_3$ and probably also La$_2$Zr$_2$O$_7$ are formed. These phase(s) are already detectable after 35 hours at 750°C, but only to a very limited extent. They become clearly visible after 10 hours at 850°C.

![Figure. 4. LSCFO microelectrodes of nominal diameter 60 μm under an optical microscope.](image)

The current-voltage characteristics of the microelectrodes was obtained by using a Potentiostat 283 (EG&G Princeton Applied Research) and impedance measurements were performed with an AIS Alpha High Resolution Dielectric Analyzer (Novocontrol, Germany). Silver paste was applied to the back side of the YSZ as a counter-electrode. Electrical contact with the micro- and counter-electrodes was established by two probe needles of a Pt/Ir-alloy with a nominal tip radius of 2.5 micrometers, which could be positioned accurately by micromanipulators (Karl Süss, Germany) under a high-resolution optical microscope (Mitutoyo, Japan). The sample was placed on top of a heating stage (Linkam, UK) and measured in air. The temperature of the sample surface was determined with an infrared pyrometer (Heitronics, Germany) after the emissivity of the individual samples had been measured as a function of temperature. Since the area of the microelectrodes is orders of magnitude smaller than the area of the counter-electrode, it can readily be assumed that the effect of the counter-electrode on the measurement results is negligible, i.e., a reference electrode can be omitted.

A typical impedance spectrum consists of an axis intercept on the high frequency side ($R_1$) and a nearly perfect semicircle of diameter $R_2$ at low frequencies. An additional, small semicircle at intermediate frequencies became visible at low temperatures ($\approx$ 500-600°C), which will not be considered in the following. This shape of the spectra is in line
with that reported for Sr-doped LaCoO$_3$ thin films (14-17). Accordingly, the large resistance $R_2$ is attributed to the oxygen reduction reaction taking place at the electrode/gas interface (electrode surface) and the corresponding capacitance $C$ is a chemical capacitance reflecting stoichiometry (i.e. oxygen vacancy concentration) changes in the microelectrode.

The effect of bias on $R_2$ and $C$ is shown in Fig. 5. Cathodic as well as anodic bias reduce the electrode resistance $R_2$ considerably: ± 200 mV for example lowers $R_2$ to about 10% of its original value. The capacitance is being enhanced by cathodic and reduced by anodic bias. This is understandable since applying a cathodic bias corresponds to a reduction of the oxygen partial pressure and thus to an increase of the vacancy concentration and the chemical capacitance. An anodic bias acts in the opposite way.

![Figure 5. Effect of cathodic and anodic dc bias on $R_2$ and $C$ in the reversible regime; each data point represents an average over 3 different electrodes.](image)

Up to about ± 200mV bias the effect of the applied voltage was essentially reversible. At higher voltages, however, the electrochemical properties of the electrode surface are changed, i.e. the values of $R_2$ and $C$ measured after application of the dc bias differ significantly from the ones measured before. This effect is described in detail in Ref. (18). Here we only present the current voltage characteristics obtained after such bias-induced changes of the electrode. Fig. 6 displays the Tafel-plot for a voltage scan between −1V and 1V. Please note that due to the ohmic drop in the electrolyte the overpotential $\eta$ at the electrode is smaller than the applied voltage. A Tafel line with a slope of 1.2 F/RT is found in the anodic regime and Tafel–like behavior also occurs in cathodic direction below $|\eta| = 400$ mV with a slope of 1.0 F/RT. A comparison with Eq. [4] shows that these slopes are very close to those expected for the rate limiting step $O^{ad} + e^- \rightarrow O^{ad}_-$ at buffered surfaces (i.e. moderate equilibrium surface coverage of $O^{ad}_-$) if $\alpha = \frac{1}{2}$ is assumed according to Marcus' theory (5-10). Other scenarios such as rate limiting adsorption or ion transfer into the electrolyte would lead to very different I-V
curves (4, 19, 20) and thus cannot explain these results. However, for a final mechanistic conclusion, further measurements, e.g. on the partial pressure dependence of the exchange current density, are required and will be performed in the future.

**CONCLUSIONS**

A model has been derived that quantifies the kinetics of electron transfer at electrode/gas interfaces. Such a new model renders necessary since the applied overpotential does not represent the electrostatic potential step change at the relevant electrode/gas interface. This model shows that the equation $I = I_0 \exp\left(\frac{3aV}{RT} - \exp\left(-\frac{\beta V}{RT}\right)\right)$ is in general not applicable to electrode/gas interfaces. In buffered systems with high adsorption site concentration and moderate surface coverage, for example, an additional factor of two appears in the exponents indicating that the relevant electrostatic potential step at the surface differs from the applied overpotential. Experiments with well-defined La$_{0.6}$Sr$_{0.4}$Co$_{0.8}$Fe$_{0.2}$O$_{3.5}$ microelectrodes showed a Tafel-like behavior in the I-V characteristics with a slope close to $F/RT$ both in the anodic and in the cathodic regime. According to our model calculations, this result would be consistent with the electron transfer $O_{ad} + e^- \rightarrow O_{ad}^{-}$ as rate limiting step in the oxygen reduction reaction.

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