MIXED CONDUCTING POROUS SOFC CATHODES: CURRENT DISTRIBUTIONS AND POLARIZATION RESISTANCES

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ABSTRACT

Numerical multidimensional simulations are presented that deal with the effect of material parameters on the current distribution in porous mixed conducting solid oxide fuel cell cathodes where the oxygen incorporation into the electrolyte takes place through the bulk of the electrode. In particular, it is demonstrated that, depending on the ratio $kq/Dq$ (surface incorporation factor/diffusion coefficient of oxide ions), different regimes can be distinguished: For large $kq/Dq$ values, only small regions close to the three-phase boundaries are relevant with respect to the oxygen reduction; a decreasing $kq/Dq$ ratio activates an increasingly larger portion of the cathode. The impact of geometrical parameters (grain size, three-phase boundary length, surface area, etc.), and thus suggested optimum geometries, depend on $kq/Dq$. The simulations showed that either porous cathodes with high surface areas (for low $kq/Dq$) or composite cathodes (for high $kq/Dq$) are recommended to achieve low polarization resistances.

INTRODUCTION

Mixed ionic and electronic conducting cathodes (MIECs) are considered to be very attractive for solid oxide fuel cells (SOFCs) because they allow oxygen reduction and incorporation into the electrolyte to occur not only via the surface of the cathode (three-phase boundary [3PB] mechanism) but also through the electrode bulk (bulk path), thus lowering the polarization resistance. However, porous cathodes exhibit a complex geometry/morphology, and even if all relevant transport and reaction parameters of the elementary electrochemical reaction steps are known, it is frequently not trivial to predict how the interplay of material properties and geometry (porosity, particle size, electrode thickness, etc.) affects the polarization resistance. Modeling studies are therefore very useful to understand the relations between performance and relevant parameters in more detail and to suggest parameters that primarily should be optimized to reduce the electrode polarization.

Calculations of the polarization resistance of MIECs are so far mainly based on a one-dimensional continuum model (1–4) assuming a homogeneous effective cathode phase that combines gas diffusion, electrochemical reaction, ion conduction, and electron conduction. Recently, simulations of the two-dimensional current distribution in mixed conducting cathode particles have been presented for the case where transport of oxide ions through the cathode bulk is rate-limiting (5,6). It has, for example, been discussed whether the electrochemically active zone of the cathode broadens if the ionic...
conductivity of the electrode is enhanced. In this contribution, we extend these calculations to cases in which the oxygen incorporation into the cathode significantly influences the overall reaction rate. The current distributions and the relations between geometrical properties and polarization resistance are discussed for different material parameters, and conclusions are drawn with respect to optimized cathode geometries. The calculations are compared with the results of a one-dimensional continuum model.

**MODEL ELECTRODE**

The model electrode considered in this paper is shown in Figure 1. It consists of pillars of a mixed conducting solid; the entire side walls of the pillars are in contact with gas. It is assumed that only the bulk path (i.e., oxygen incorporation into the cathode) contributes to the overall oxygen reduction rate. The oxygen incorporation reaction into the cathode is described by an electrical surface exchange coefficient, $k^d$. The ionic transport through the bulk of the electrode is determined by the ionic conductivity of the MIEC $\sigma_{\text{ion}}$, which is related to the self-diffusion coefficient $D^q$ of oxide ions via the Nernst-Einstein equation $D^q = (kT\sigma_{\text{ion}})/(4e^2c)$ ($c$, $k$, $T$, and $e$ are oxide ion concentration, Boltzmann constant, temperature and elementary charge, respectively).

![Sketch of the model system consisting of a mixed conducting cathode (contacted by a current collector at the top), a thin electrolyte with negligible resistance, and a reversible counter-electrode. The potential distributions in cross sections of the dark regions A and B are shown in Figure 2.](image)

Figure 1. Sketch of the model system consisting of a mixed conducting cathode (contacted by a current collector at the top), a thin electrolyte with negligible resistance, and a reversible counter-electrode. The potential distributions in cross sections of the dark regions A and B are shown in Figure 2.

The gradient of the electrochemical potential of the electrons is assumed to be negligible (very high electronic conductivity of the MIEC). As discussed in Ref. (5),

$$\text{div}(\text{grad} \tilde{\mu}_e) = 0 \quad [1]$$
must be solved under boundary conditions \( \nabla_n \bar{\mu}_v (\text{MIEC}_f) = k^4/D^4 (2eU - \bar{\mu}_v (\text{MIEC}_f)) \) and \( \bar{\mu}_v (\text{CE}) = 0 \) in order to obtain the electrochemical potential of oxygen vacancies \( \bar{\mu}_v \) in the sample. (CE denotes the reversible counter electrode, \( \nabla_n \) refers to the gradient normal to the surface, \( U \) the applied voltage, and MIEC\(_f\) indicates the free surface of the MIEC; the equilibrium electrochemical potential of vacancies is set to zero.) From \( \nabla \bar{\mu}_v \) the ionic current and thus the polarization resistance of the sample can be determined.

The finite element software FLUXEXPERT (SIMULOG, France) was applied to numerically calculate \( \bar{\mu}_v \) and the effective, area-related polarization resistance, \( R \). More information on these simulations can be found in Refs. (5,7).
RESULTS AND DISCUSSION

For a fast oxygen surface reaction \( (k^d/D^q >10^3/L_p) \), the oxygen incorporation into the cathode mainly occurs close to the 3PB (Figure 2a) because that enables the oxide ions to diffuse along the shortest possible paths through the MIEC. Hence, very inhomogeneous current density distributions result (Figure 3). This has been discussed in Refs. (5, 6) for a quasi two-dimensional model electrode, and only one aspect shall be emphasized: An interpolation formula (5,7,8) allows one to calculate the minimum ionic conductivity that is required to achieve acceptable cathodic polarization resistances. Surprisingly, an ionic conductivity as low as \( = 5\times10^{-5} \text{ S/cm} \) results for submicrometer sized particles. Since the ionic conductivity in the cathode is strongly bias-dependent (ionic transport in the MIEC can be described by Hebb-Wagner’s theory of stoichiometry polarization [9-11]) and a cathodic overvoltage of ca. 80 mV is still acceptable, even an equilibrium value of 2\( \times10^{-5} \text{ S/cm} \) may be sufficient. Calculations in (12) showed that composites can reduce the polarization resistance by at least a factor of 10 if the electrochemical reaction occurs close to the 3PB. It can therefore be concluded that composite cathodes consisting of electrolyte particles and mixed conducting particles with an ionic conductivity as low as ca. 2\( \times10^{-6} \text{ S/cm} \) may be sufficient to make acceptable porous SOFC cathodes. Consequently, mixed conductors with ionic conductivities of the order of 10\( ^3 \text{...}10^4 \text{ S/cm} \) reported e.g. for \( \text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.9}\text{Co}_{0.1}\text{O}_3 \) compounds at 800°C (13-17) are, from a transport point of view, not required. Even the rather poor ion-conducting doped \( \text{LaMnO}_3 \) could be considered to be a MIEC with sufficiently active bulk path if its ionic conductivity were enhanced by about two orders of magnitude; this might be achieved by co-doping, for example, with Fe.

However, these considerations are only valid for fast oxygen incorporation reactions into the cathode, and the potential and current distribution drastically changes if \( k^d \) is lowered (Figures 2b and 3). To minimize the unavoidable increase of the polarization resistance, an increasing fraction of the surface significantly contributes to the electrochemical

![Graph showing current density distribution](image)

**Figure 3.** Normal component of the current density distribution along the surface of the first particle layer (black bold lines in Figure 2 (a) and (b)) on a logarithmic scale for \( k^a \to \infty \) and \( k^d/D^q = 62.5 \text{cm}^2/\text{s} \); \( \sigma_{\text{ion}} = 10^{-3} \text{ S/cm} \).
reaction even though this is accompanied by larger distances ions have to diffuse in the MIEC. Therefore, the potential distribution penetrates into the mixed conducting cathode (Figure 2b) and the incorporation current density distribution flattens (Figure 3).

The smaller \( k^q \) is the larger the portion of the cathode surface that significantly contributes to the oxygen reduction reaction. (Note that the relevance of a specific part of the surface depends on the relative current fraction that it contributes to the overall current; hence, a surface region can be unimportant for certain \( k^q \) values even though, on the absolute scale, it incorporates more ions than in a case where it is relevant.)

Figure 4 displays the resulting relation between the area-related polarization resistance, \( R \), and \( k^q/D^q \). Depending on the ratio of \( k^q/D^q \) of the mixed conducting cathode, four regimes can be distinguished (7): For \( k^q/D^q \) values much larger than the inverse particle size (regime I), only small regions close to the 3PBs are relevant with respect to the oxygen reduction. A decreasing \( k^q/D^q \) ratio activates an increasingly larger portion of the cathode, i.e., the area of the MIEC surface that is of importance for the oxygen reduction reaction monotonically increases. In regime II (\( L_{pk^q/D^q} \) values between 1 and 1000), it is still mainly the first particle layer that contributes to the oxygen reduction; \( L_{pk^q/D^q} \) values < 1 lead to a deeper penetration of the relevant ionic current into the cathode (regime III), and eventually the entire cathode surface is involved in the oxygen reduction reaction (regime IV). Each regime exhibits a characteristic dependence of the polarization resistance on surface reaction coefficient, ionic conductivity, and particle size. More details with respect to these relations are given in Ref. (7).

While regimes I and II certainly require calculations of the local current distributions within single particles, regimes III and IV might also be modeled on a one-dimensional continuum level (1-4). In order to verify such a one-dimensional approach the corresponding area-related polarization resistance of a mixed conducting cathode derived from Eq. (34) in Ref. (2)

\[
R = \frac{kT}{4e^2 \sigma_{\text{ion}}} \left[ \frac{\tau}{k^q D^q \phi_{\text{vol}}} \coth \left( \frac{k^q }{D^q \phi_{\text{vol}}} \right) \right] \tag{2}
\]

is compared with our numerically obtained solution. (Eq. [2] in the limit of \( \coth(x) \to 1 \) has also been deduced in Ref. (1). Symbol \( \tilde{a} \) denotes the surface area per volume element, \( \phi_{\text{vol}} \) the volume fraction of the mixed conductor; \( \tau \) is known as tortuosity and takes account of the fact that current paths in the cathode are multi-dimensional; it is essentially defined by the relation between effective ionic conductivity \( \sigma_{\text{eff,ion}} \) of the porous MIEC network and the ionic conductivity \( \sigma_{\text{ion}} \) (\( \sigma_{\text{eff,ion}} = \phi_{\text{vol}} \sigma_{\text{ion}}/\tilde{a} \)). In many cases, \( \tau \) is not easily available for a given porous structure; in our case, however, finite element calculations yielded a value of \( \tau = 1.48 \). In Figure 4 the polarization resistance according to Eq. [2] with \( \tilde{a} = (15\pi)/(32L_\Phi) \) and \( \phi_{\text{vol}} = 5\pi/32 \) is compared with the numerically calculated “exact” polarization resistance. The continuum model yields a good approximation to the true polarization resistance in regimes III and IV. Cases where mainly the first particle layer is involved (regimes I and II), however, cannot be treated in such a one-dimensional manner.
Figure 4. Area-related polarization resistance of model cathode for different $k^q/D^q$ ratios; $L_p = 1.6$ μm, $\sigma_{\text{ion}} = 10^3$ S/cm. Four different regimes (I-IV) can be distinguished. The circles indicate the polarization resistance calculated from the continuum model according to Eq. [2].

It turns out that the geometry dependence of the polarization resistance is considerably influenced by the ratio $k^q/D^q$: for low $k^q/D^q$ values the surface area per volume $\tilde{a}$ is the most decisive geometrical parameter; for large $k^q/D^q$ values (regime I), however, $R$ is almost inversely proportional to the 3PB length; Hence also suggestions of optimized microstructures depend on the regime: For $L_p k^q/D^q < 1$ the surface area of the porous structure should be high (small particles) while for oxygen incorporation mainly at the 3PB ($L_p k^q/D^q \gg 1$) the 3PB length should be as large as possible which means that a composite electrode is recommended in the latter case.

CONCLUSIONS

Exact calculations of the potential distributions in mixed conducting cathodes showed that, depending on the ratio $k^q/D^q$, four regimes can be distinguished: For $k^q/D^q$-values much larger than the inverse particle size $L_p$ (regime I) only small regions close to the three phase boundaries are relevant with respect to the oxygen reduction. A decreasing $k^q/D^q$ ratio “activates” an increasingly larger portion of the cathode, i.e., the area of the MIEC surface that is involved in the oxygen reduction reaction monotonically increases: In regime II ($L_p k^q/D^q$-values between 1 and 1000), it is still mainly the first particle layer that contributes to the oxygen reduction; $L_p k^q/D^q$-values < 1 lead to a penetration of the ionic current into the cathode network (regime III), and finally the entire cathode surface is of importance (regime IV). Regimes III and IV can satisfyingly be described by a one-dimensional continuum electrode model. The simulations also showed that, depending on
k^3/D^4, either porous cathodes with high surface areas (for low k^3/D^4) or composite cathodes (for high k^3/D^4) are recommended to lower the polarization resistance.

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