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Viewpoint Paper

The determination of the three-phase boundary width of solid oxide fuel cell cathodes by current-driven ^{18}O tracer incorporation

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Abstract—For several electrode materials oxide ion incorporation into a solid electrolyte is believed to take place in a narrow zone close to the three-phase boundary (TPB). However, a determination of the width, exact location and distribution of the electrochemical activity of this incorporation zone is difficult. We discuss how far current-driven oxygen tracer experiments allow a quantification of TPB properties. The considerations are exemplified by experiments revealing the TPB width of Pt on YSZ.

Keywords: Ionic conductors; Diffusion; Interfaces; Oxides

1. Introduction

The three-phase boundary (triple-phase boundary, TPB) of a solid oxide fuel cell (SOFC) cathode, i.e. the line where oxygen, electrode and electrolyte meet, is believed to be the center of the electrochemical activity of cathode materials with little oxygen permeability, such as Pt or Au and, depending on the experimental conditions, often also Sr-doped $LaMnO_3$ (LSM) [1–9]. However, the zone where oxide ions are incorporated into the electrolyte can hardly be an ideal one-dimensional line and a certain spatial extension, termed the "TPB width", has therefore been hypothesized. Some of the mechanisms leading to a broadening of the TPB are surface diffusion of ionized species on the electrolyte, electron conduction in the electrolyte and fast diffusion of oxygen species along the electrode/electrolyte interface. Conceptually such considerations are well established, but the exact width of the oxygen incorporation zone or the decay length of the incorporation current density along the solid electrolyte surface is still largely unknown. Equally unknown is the direction into which the TPB extends; it might spread along the free electrolyte surface or along the electrode/electrolyte interface, or both.

In principle, experiments on incorporation of an oxygen isotope tracer (^{18}O) into an oxide can not only yield kinetic parameters, such as the surface exchange coefficient or the diffusion coefficient (k^* or D^*, respectively; see e.g. De Souza and Kilner [10], Lane et al. [11], Sayers et al. [12] and Wagner et al. [13]), but may also reveal information on the location of active incorporation zones. In particular current-driven ^{18}O incorporation and subsequent visualization of the resulting ^{18}O images by secondary ion mass spectrometry (SIMS) was shown to be a highly attractive method of obtaining information on electrochemically active sites of cathodes such as Sr-doped $LaMnO_3$, Pt or Au [14–20]. In contrast to conventional oxygen tracer exchange studies, the latter experiments relied on voltage as the driving force to enhance the ^{18}O concentration in the sample. Tracer experiments under applied electrical fields have been discussed in the literature for many decades [21–23], but the experiments mentioned above [14–20] introduced a very novel aspect: the crucial effect of the electric field was oxygen incorporation (^{18}O injection), rather than its contribution to the driving force of oxide ion motion in the electrolyte.

Even though this tool of current-driven tracer incorporation might help solve several questions on the width and extension of the TPB zone, unambiguous quantitative studies are still lacking. This is partly related to the problem that after being electrochemically pumped into the electrolyte ^{18}O also diffuses in the bulk and this diffusion may broaden the ^{18}O enriched zones. Experimentally determined ^{18}O images and profiles might thus primarily reflect bulk diffusion rather than the true TPB width or decay of the electrochemical incorporation activity along the electrolyte surface. This bulk diffusion is problematic not only during quenching of the resulting profiles but also during the electrochemical pumping itself [24]. It was shown that a peak in ^{18}O concentration may remain close to the TPB despite diffusive broadening and thus active zones may indeed be identified [17]. However, it remained unclear whether quantitative information on the TPB

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width or on the incorporation decay length can also be obtained.

It is the objective of this paper to reconsider the approach of current-driven ^{18}O injection from a quantitative point of view and to discuss how far quantification of TPB parameters is possible by this method. The role of ^{18}O diffusion and ^{18}O field migration in the electrolyte during the electrochemical pumping process is quantified and limits are given within which quantitative experiments may be realistic. These considerations are experimentally exemplified for the system O_2/Pt/yttria-stabilized zirconia (YSZ).

2. Relevance of ^{18}O bulk diffusion in the electrolyte

In order to understand how ^{18}O bulk diffusion during electrochemical pumping of ^{18}O into an electrolyte affects the resulting tracer profile we first consider estimates of diffusion lengths. In a one-dimensional (1D) experiment the diffusion lengths L_D of ^{18}O tracer ions can be calculated from the tracer diffusion coefficient D^* and the diffusion time t according to:

$$L_D = \sqrt{D^* t} \tag{1}$$

Tracer diffusion coefficients can be estimated from the ionic conductivity (σ_{ion}) via [25]:

$$D^* = \frac{f_c kT}{4e^2 n_0}\sigma_{ion} \tag{2}$$

In idealized cases f_c denotes the correlation factor (0.65 for cubic zirconia [26]), e, k, T are the elementary charge, Boltzmann's constant and temperature, respectively, and n_0 corresponds to the concentration of oxide ions in the electrolyte. Table 1 summarizes some 1D diffusion lengths in YSZ calculated from the ionic conductivity and Eq. (2) for different diffusion times and temperatures. Conductivity was measured by impedance spectroscopy on 9.5 mol.% Y_2O_3 doped single crystals [27]. It becomes immediately clear that ^{18}O diffusion is very fast at typical SOFC operation temperatures. At 700 °C, for example, a diffusion length of 1.6 μm results after 1 s. Monitoring a TPB with a width of a few 100 nm by current-driven tracer incorporation is thus expected to be very difficult at such high temperatures. Even very quick incorporation experiments and immediate subsequent quenching cannot avoid a strong broadening of the resulting ^{18}O profile due to ^{18}O diffusion in YSZ.

Table 1. ^{18}O tracer diffusion coefficients calculated from ionic conductivity data on YSZ single crystals [27] and the resulting diffusion lengths for several times and temperatures.

Temperature (°C)	Time (s)	Diffusion coefficient ($cm^2\ s^{-1}$)	Diffusion length $L_D = \sqrt{D^* t}$
700	60	2.5×10^{-8}	12.2 μm
500	60	9.4×10^{-10}	2.4 μm
255	60	2.5×10^{-13}	39 nm

In order to further quantify the true (i.e. non-one-dimensional) problem, numerical finite element calculations were performed for the model geometry sketched in Figure 1a. An active zone, symmetrically located around the TPB, is assumed to incorporate oxide ions during cathodic current flow. As shown in Figure 1b and c, two different types of TPB activity were assumed: first, a constant particle flux density J_{inc} (tracer incorporation) was used along the entire TPB width W_{TPB}; second, exponential decay of the incorporation flux density along the electrolyte surface was considered. The decay of activity takes account of kinetic situations in which slow transport processes at or close to the surface limit broadening of the oxygen incorporation zone. Those processes could be surface diffusion of ionized species on the electrolyte, electron conduction in the electrolyte or diffusion of oxygen species along the electrode/electrolyte interface. Sites close to the TPB have a better supply of the kinetically relevant particles (oxygen species or electrons) compared with sites far from the TPB and a decay of J_{inc} results. Even though in general the decay is not necessarily exponential, an exponential shape of J_{inc} should reflect the main features of such situations.

An $^{18}O_2$ concentration of 100% in the gas during the entire "experiment" and 0% ^{18}O in the electrolyte before electrochemical pumping was used in these calculations. The diffusion equation

$$\frac{\partial \bar{c}_{^{18}O}}{\partial t} = D^* \mathrm{div}(\mathrm{grad}(\bar{c}_{^{18}O})) \tag{3}$$

was solved for the normalized tracer concentration (i.e. the ^{18}O isotope fraction)

$$\bar{c}_{^{18}O} = \frac{n_{^{18}O}}{n_0} \tag{4}$$

($n_{^{18}O}$ is the ^{18}O concentration) under the boundary condition

$$J_{inc} = -D^* n_0 \frac{\partial \bar{c}_{^{18}O}}{\partial y} \tag{5}$$

along the TPB. For sufficiently high polarization and thus negligible tracer release current density i_{out} (O^{2-} oxidation) the tracer incorporation current density i_{inc} equals the y component of the effective current density in the TPB zone $i_y = i_{inc} - i_{out}$ and J_{inc} is given by:

$$2eJ_{inc} = i_{inc} \approx i_y \tag{6}$$

Here the cathodic current densities are taken as negative, in contrast to related calculations made in Fleig [24].

Figure 2 shows cross-sections of the resulting tracer concentration profiles for a true TPB width of 500 nm (constant J_{inc}) and diffusion coefficients of 2.5×10^{-8} and 2.5×10^{-13} $cm^2\ s^{-1}$, corresponding to temperatures of 700 and 255 °C, respectively. The cathodic incorporation of tracer ions with a current density i_{inc} of -180 mA cm^{-2} for 700 °C and -18 μA cm^{-2} for 255 °C was assumed to last 60 s. These plots clearly visualize

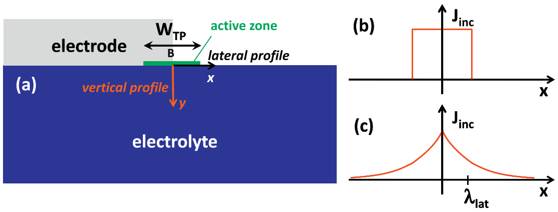

Figure 1. (a) Sketch illustrating the geometry of the model used in the finite element calculations. (b, c) The two shapes of the oxygen incorporation flux density J_{inc} along the electrochemically active zone.