AGEING OF SOLID OXIDE FUEL CELLS BASED ON ZIRCONIA OR OTHER OXIDE ELECTROLYTES

G. Petot-Ervas and C. Petot
Laboratoire SPMS, UMR 8580
Ecole Centrale Paris
92295 Châtenay-Malabry, Cedex, France

ABSTRACT

This work concerns the ageing of solid oxide fuel cells in operative conditions due to matter transport processes, which occur in the electrolyte and oxide electrode material cationic sublattice. The surface stability and kinetic demixing processes in presence of chemical potential gradients through the materials are reviewed. Available experimental results concerning yttria-doped zirconia and iono-covalent oxides are reported. These results are discussed in relation with the microstructure and composition changes near the electrolyte-electrode material interfaces.

INTRODUCTION

To improve the performance of fuel cells, compounds with higher conductivities are required (1,2). However, it is now recognized that the electrolyte/electrode interfaces play a major role in determining the cell characteristics (1,3-6). Indeed, the charge transfer reactions occur at this interface and the kinetics as well as the degree of reversibility of these exchange reactions control in part the internal resistance of the cell. The knowledge of the microstructure and composition of the electrolyte/electrode interfaces and their evolution as a function of time is thus crucial to control the ageing of the electrochemical cells and to optimise their operation conditions.

This paper reviews the principle of the cation redistributions, the so-called kinetic demixing process, which occur in a multicomponent compound exposed to a "generalized" thermodynamic potential gradient (7-9). Emphasis is given to the behaviour of solid electrolytes and semiconducting oxides, in the presence of a chemical potential gradient, an applied electrical field or a stress gradient. Kinetic demixing results obtained for yttria-doped zirconia and iono-covalent oxides are reported. The stability of the surfaces under non-equilibrium conditions is also discussed in relation with the microstructure of the interfaces and the electric contact at the electrode level.

GENERAL EQUATIONS

In a general way, if one neglects the correlation effects, one can assume that the flux of charged species "i" in an ionic compound is due mainly to the electrochemical potential gradient (\nabla \eta_i). In the "z" direction, this flux may be written, with respect of the laboratory reference frame (7-9):

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where $\frac{\partial \eta_i}{\partial z}$ is the electrochemical potential gradient of the charged species $i$, related to it chemical potential gradient, $\frac{\partial \mu_i}{\partial z}$, by the well known equation:

$$J_i = -\frac{C_i}{RT} D_i \frac{\partial \eta_i}{\partial z}$$

[1]

where $\frac{\partial \eta_i}{\partial z}$ is the electrochemical potential gradient of the charged species $i$, related to its chemical potential gradient, $\frac{\partial \mu_i}{\partial z}$, by the well known equation:

$$\frac{\partial \eta_i}{\partial z} = \frac{\partial \mu_i}{\partial z} + Z_i f \frac{\partial \Phi}{\partial z}$$

[2]

$f$ is the Faraday constant, $C_i$ the concentration of the charged species $i$ per unit volume, $Z_i$ its electrical charge, $D_i$ its diffusion coefficient, $\Phi$ the local electrical potential and $\frac{\partial \Phi}{\partial z}$ the Nernst field, due to the difference of mobility of point defects and of electronic defects in the absence of an applied electric potential.

Because ions require defects to move, the transport processes can be described considering either the flux of the point defects ($J_d$) or that of the ions ($J_{ion}$), coupled through the condition,

$$J_d + \Sigma J_{ion} = 0$$

[3]

In materials involved in electrochemical cells the prevailing defects are generally present on the anionic sublattice. The cationic diffusion is then lower than the anionic diffusion but it cannot be neglected because it can cause chemical and microstructural changes at the interface level, as we shall see in the next sections.

**Transport Processes on the Anionic Sublattice in Deficient Oxygen Oxides**

In oxide fuel cells, the solid electrolyte, such as stabilized zirconia, is used in combination on its opposite sides with an electronic conducting material connected to the electrical junctions. This arrangement allows the interfacial reactions with the surrounding atmosphere to take place ($O_2 \leftrightarrow V_{O^\bullet} + 2e^- + \frac{1}{2} O_2$). The fuel (e.g. hydrogen) is oxidized at the anode and the oxidant (e.g. oxygen) is reduced at the cathode. These reactions can occur due to the diffusion of oxygen ions across the electrolyte, while the electrons flow from the anode to the cathode, via the external circuit, producing direct-current electricity. The oxygen transport across the solid electrolyte is then the rate-determining step of the oxidation or reduction reactions at the interfaces. In such arrangement, the kinetic demixing processes can be of concern to the electrolyte as well as to the electrode material.

For a quantitative description of the transport processes, it is convenient to cast Eqn. 1 in a form that includes the most readily accessible parameters, i.e. the oxygen partial pressure and the composition. For simplicity, we will consider an ideal solid solution ($AO_2$, $BO_Y$, in which the prevailing defects are isolated oxygen vacancies ($V_{O^\bullet}$). For both a semiconducting oxide ($C_0D_0 \ll C_pD_p$) or an ionic compound ($C_0D_0 \gg C_pD_p$), whose opposite sides are in equilibrium with different oxygen partial pressure, one can show
according to Eqn.3, that Eqn.1 can be written (10, 11) as:

\[ J_{O^--} = -\frac{C_0 D_0}{RT} \frac{\partial \mu_{O^-}}{\partial z} \]

with \( \frac{\partial \mu_{O^-}}{\partial z} \) \[ \frac{\partial n_{AO_2}}{\partial z} + 2F \]

\[ \frac{\partial n_{BO_2}}{\partial z} \gamma + \gamma F \]

\[ \frac{\partial n_{AO_2}}{\partial z} + 2F \]

\[ \frac{\partial n_{BO_2}}{\partial z} \gamma + \gamma F \]

\[ \frac{\partial n_{AO_2}}{\partial z} + 2F \]

\[ \frac{\partial n_{BO_2}}{\partial z} \gamma + \gamma F \]

Transport Processes on the Cationic Sublattice in Deficient Oxygen Oxides

We have considered the ideal solid solution (AO_2,BO_y) and we have assumed that the prevailing cationic defects in the host oxide AO_2 are cationic vacancies "α" time ionised (V_A^α). In view of the virtual chemical equilibrium between ions and neutral species (AO_2<>A^{4+}+2O^2_, BO_y<>B^{α+y}O^{2-y}_2, with \( \gamma = \alpha/2 \)), one can show that the cationic fluxes can be written as

\[ J_{A^{4+}} = -\frac{D_A C_A}{RT} \frac{\partial n_{A^{4+}}}{\partial z} = D_A C_A \left[ \frac{\partial n_{AO_2}}{\partial z} + 2F \right] \]

\[ J_{B^{α+y}} = -\frac{D_B C_B}{RT} \frac{\partial n_{B^{α+y}}}{\partial z} = D_B C_B \left[ \frac{\partial n_{BO_y}}{\partial z} \gamma + \gamma F \right] \]

These equations allow the problem of matter transport under a generalized thermodynamical potential gradient to be reduced to a problem of diffusion under a driving force \( R = RT\tilde{\gamma} \).

When the sample is exposed, at constant temperature, to an oxygen chemical potential gradient, one can show, from the equation of formation of the defects (O_O<>V_{O^-} + 2e^- + 1/2 O_2), that \( \tilde{R} \) may be written as

\[ \tilde{R} = RT\tilde{\gamma} = \frac{\partial \mu_{O^-}}{\partial z} = -3RT \frac{d \ln \left[ \frac{V_{O^-}}{T} \right]}{dz} \]

While in presence of an applied electrical field U/L (8-10)

\[ \tilde{R} = \frac{Z_i e U}{L} \]

and in presence of an applied stress \( \sigma \), leading to diffusional creep (8-10):

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where $Z_i$ is the electrical charge of the ions and $C_M$ the overall concentration (mol cm$^{-3}$) of oxygen sites in the lattice.

**Remark:** If the compound AO, BO$_8$ is not an ideal solid solution, the driving force related to the activity coefficient $\gamma$ ($RT \partial \ln \gamma / \partial z$) must be added to the second term of Eqns. [6] and [7]).

The driving force $R$ leads to a shift velocity of the cations A$^{2+}$ and B$^{2+}$, with respect to the laboratory reference frame, given by (7-12)

$$v_{A^{2+}} = J_{A^{2+}} / C_{A^{2+}} \quad \text{and} \quad v_{B^{2+}} = J_{B^{2+}} / C_{B^{2+}}$$

Consequently, a concentration gradient $\partial x / \partial z$ develops progressively through the sample, assumed initially homogeneous, if the diffusion coefficients of the cations A$^{2+}$ and B$^{2+}$ are different ($D_A \neq D_B$).

Furthermore, if one neglects the influence of the changes of composition on the surfaces and if one assumes that these end surfaces are in equilibrium with the surrounding atmosphere, the vacancy concentration on these surfaces can be assumed constant. This local chemical equilibrium is in fact a dynamical steady state, since there is in permanence an irreversible flow (in or out) of vacancies coupled to an irreversible flow of cations on the boundary regions. This leads to the creation of lattice sites near the surface where the cations arrive and to their annihilation on the opposite side. As a result, a shift of the end surfaces occurs in the same direction of the cationic fluxes, with a velocity (if one neglects the small changes of volume due to the concentration variations), which is given by (7-9).

$$v = \frac{J_A + J_B}{C_M(x_A + x_B)} = -C_M \frac{J_V}{1 - x_V} = -J_V / C_M$$

**Remark:** When the prevailing defects are present on the cationic sublattice, the same relations hold for the cationic fluxes.

In presence of an oxygen chemical potential gradient and if the prevailing defects are cationic vacancies $\alpha$ time ionised ($V^\alpha_A$), one obtains, at $T = ct$ (8-9),

$$R = RT \frac{d\mu}{dz} = -RT(1+\alpha) \frac{d \ln V^\alpha_A}{dz}$$

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EXPERIMENTAL RESULTS

Kinetic Demixing and Morphological Stability of Surfaces in Semiconducting Oxides Exposed to a Chemical Potential Gradient

In order to illustrate the importance of the kinetic demixing and the morphological changes of the surfaces, we will report first experimental results obtained with a Co$_x$Mg$_{1-x}$O solid solution (7-9). This material can be considered as a model semiconducting oxide. Indeed, it is an ideal solid solution and there exists the diffusion and thermodynamic data necessary to do calculations.

Simulation of the concentration profiles. The time dependence of the kinetic demixing was calculated by substituting the expression for the cationic fluxes (Eqns. [6], [7] and [9]) in the continuity equation (\(dx_j/dt = -\text{div } J_i/C_M\)). As an example, Figure 1 simulates the development of the kinetic demixing, at 1439°C, in a Co$_x$Mg$_{1-x}$O solid solution with an initial homogeneous composition \(x_{Mg} = 0.49\), exposed suddenly, at \(t = 0\), to an oxygen potential gradient included between \(P_{O_2} = 0.21\) bar and \(P_{O_2} = 0.07\) bar. As shown in Figure 1, the calculated profile (8, 9) for a time of 136 h is in good agreement with the experimental data obtained by Schmalzried et al. (7).

![Figure 1](image)

Figure 1. Kinetic demixing in a Co$_x$Mg$_{1-x}$O sample annealed at 1439°C, under an oxygen potential gradient included between 0.07 and 0.21 bar; (a) Calculated time evolution of the kinetic demixing (8, 9), (b) Comparison with the experimental results obtained by Schmalzried (7).

Of course, when a semiconducting oxide is used as electrode material, a change in the surface composition can lead to an evolution of the electrode resistance. In some cases, the kinetic demixing processes can lead to the precipitation of impurities or to the decomposition of the compound, as it has been observed for Ni$_2$SiO$_4$ (11), for example.
As shown in Figure 2, precipitates of NiO appear near the surface of the silicate in contact with the high oxygen partial pressure (a), while a continuous layer of SiO₂ has formed on the opposite surfaces (b).

**Evolution of the surface microstructure.** Figures 2 and 3 illustrate the typical microstructures of the cross sections, near the opposite surfaces of a Ni₂SiO₄ polycrystal and a CoₓMg₁₋ₓO single crystal, after a kinetic demixing process. The surface where the cations arrive remains nearly plane and it is generally considered as a stable surface. On the contrary, the opposite side shows a jagged surface. This surface is generally considered as an unstable surface (7-9), because any crack or cavity tends to develop with the arrival of the cationic vacancies. Of course, these instabilities at the electrode level can lead to a local loss of the contact between the solid electrolyte and the electrode material and to an increase of the electrode resistance.

![Figure 2. Backscattered scanning electron micrograph (after 11) of a cross section of a Ni₂SiO₄ sample exposed to an oxygen potential gradient between 0.21 and 3.1x10⁻⁴ atm at 1336°C for 96 h: (a) exposed to Pₒ₂ = 0.21 atm, (b) to Pₒ₂ = 3.1x10⁻⁴ atm.](image1)

![Figure 3. Morphology of a cross section near the surface of a CoₓMg₁₋ₓO sample, after a kinetic demixing process. A jagged surface develops near the surface where the cationic vacancies are annihilated (a) while the opposite side (b) remains nearly plane.](image2)
Kinetic Demixing and Morphological Stability of Surfaces in Ionic Conducting Oxides Exposed to a "Generalized" Thermodynamical Potential Gradient

In order to know the importance of the kinetic demixing processes in ionic conducting oxides, experiments have been performed with yttria (9 mole %)-doped zirconia single crystals. For experimental simplicity we have followed the kinetic demixing induced by an electrical field. The experiments have been performed at 1350°C, in air, with disks of uniform thickness, whose opposite sides are coated with a layer of porous platinum. The applied voltage was equal to 0.73 V and to 4 V, respectively. The demixing profiles across the sample (Figure 4), determined by EPMA analysis, show that cation redistributions occur mainly in a layer close to 10 μm near the surface.

Remark: A voltage of 4 V was applied at the terminals of the cell without decomposition of the oxide due to the high electrode resistance when platinum is used as electrode.

Calculations have also been performed using diffusion data of the literature (9). They predict a negligible concentration gradient despite the important driving force applied. As an example, after 110 days under an applied electrical field of 0.73/10^3 V/m, the yttrium concentration variation on the first monolayers near the surface is close to 500 ppm and the change in composition is lower than 100 ppm at a depth close to one micron. The difference between the calculated and experimental results may be attributed to the diffusion values we have used (11) ($D_Y = 3.44 \times 10^{-20} \text{ m}^2/\text{s}$ and $D_Zr = 1.39 \times 10^{-20} \text{ m}^2/\text{s}$) or to the correlation effects, neglected in the formal treatment (Eqns. [6] and [7]).

Figure 4. Experimental kinetic demixing profiles in yttria (9 mol% Y$_2$O$_3$)-doped zirconia single crystals, maintained under 0.73 V for 110 days and 4 V for 90 days (9).

Figure 5 shows the microstructure of the end surfaces. At the cathode, the crystal has developed inside the layer of porous platinum with the arrival of the cations. At the anode, the platinum was removed easily at the end of the experiment. This surface shows important perturbations. It is considered an unstable surface because any crack or cavity tends to develop with the arrival of the cationic vacancies (7-9). Of course, such instabilities can lead to a loss of the contact between the solid electrolyte and the electrode material and an increase of the electrode resistance. Consequently, to prevent as much as possible such effects, the surface of the solid electrolyte connected to the Electrochemical Society Proceedings Volume 2003-07
positive pole of the d.c. voltage source must be very carefully polished and a small mechanical pressure must be applied on the electrode material at the anode level.

Figure 5. Morphology of a cross section near the anode (a) and the cathode (b) surfaces of an yttria (9 mole% Y₂O₃)-doped zirconia single crystal, before it has been maintained under 0.73 V for 110 days at 1350°C.

Kinetic Demixing Under a Stress Field.

In the presence of a nonhydrostatic stress, a driving force appears in the material, which can lead to diffusional creep at elevated temperature. One can recall that diffusional creep occurs due to the transport of molecular groups (AO₂ and BO₆, for instance). Creep rate is then controlled by the slowest species. Consequently, kinetic demixing processes will be observed in materials, such as doped zirconia, in which the cationic diffusion is slow compared to the oxygen diffusion.

To our knowledge the only available experimental results have been obtained with yttria-doped zirconia polycrystals (13). The deformation was performed at a stress of 30 MPa, for 75 h, at a temperature of 1600°C. The flow law indicates that deformation occurs well by a diffusional creep mechanism (Nabarro-Herring creep), but kinetic demixing was not observed. Dimos et al. (13) attribute this result to the close diffusivities values of the cations or to extensive grain rotations during diffusional creep. However, according to the previous results obtained in the presence of an applied electrical field, the results obtained by Dimos et al. can be also explained by both the duration of the experiments and the sensitivity of the electron microprobe analysis they have used to determine the cation profiles. Consequently, if the ionic compound is maintained under a nonhydrostatic stress during a long period of time, kinetic demixing at the interfaces cannot be excluded as well at the level of both the grain boundaries and the electrodes. Of course, such effects will be all the more important as the temperature increases.

CONCLUSIONS

In this paper we have reported a formal treatment to analyse the transport processes in ionic and semiconducting oxides in the presence of a “generalized” thermodynamical
potential gradient (chemical potential gradient, electrical field and nonhydrostatic stress). The kinetic demixing processes near the electrodes as well as the morphological changes leading to surface instabilities have been analysed. The precipitation of components or impurities near the interfaces was also considered. Experimental and calculated results have been reported. These transport processes have been discussed in relation with the stability of the surfaces and the increase of the electrode resistance. The emphasis has been given to the importance of the kinetic demixing and morphological change according to the transport properties of the materials. Finally this work has been performed in order to try to understand the behaviour of the electrochemical cells under working conditions and to control and eventually to prevent their premature ageing.

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