

# Solid State Transport of Reactive Charged Particles: Application to Metal Oxidation

P. Buttin<sup>\*1,2</sup>, B. Malki<sup>2</sup>, P. Barberis<sup>3</sup>, B. Baroux<sup>2</sup>

<sup>1</sup>AREVA – AREVA NP Fuel Business Unit, 10 rue Juliette Récamier, 69456 Lyon Cedex, France ;

<sup>2</sup>Institut National Polytechnique de Grenoble, PHELMA/SIMAP/SIR, 1130 rue de la piscine, 38402 Saint Martin d'Hères, France ; <sup>3</sup>AREVA – AREVA NP – CEZUS Research Center, Avenue Paul Girod, 73403 Ugine Cedex, France

\*Corresponding author: 1130 rue de la piscine, 38402 Saint Martin d'Hères, France  
paul.buttin@simap.grenoble-inp.fr

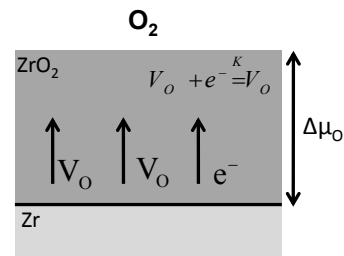
**Abstract:** This paper studies multicomponent transport through zirconia, assuming a chemical reaction involving electrons and oxygen vacancies defects. Classically, according to the Wagner theory for ambipolar diffusion, the electroneutrality condition in the oxide is considered. Therefore three constraints must be satisfied on the transport problem: oxide stoichiometry, electroneutrality and the source term coming from chemical reactions. The stoichiometry constraint prevents to solve the problem with the Nernst-Planck equation as implemented in COMSOL Multiphysics. This work is focused on a method to reduce the problems in just one transport equation keeping all constraints on the system. Simulation results from this modeling are linked to experimental oxide growth kinetics and discussed in the framework of available data in the literature.

**Keywords:** oxidation, zirconia, chemical reaction, multicomponent transport

## 1. Introduction

Understanding defects transport in oxides is a mandatory step to grasp key factors controlling metal oxidation. A way to do this is to develop a model to study multicomponent transport coupled with an internal defects reaction. Here we study multicomponent transport through zirconia, considering an anionic conductivity and taking into account the following defects:  $V_o$ ,  $V_o$ ,  $e^-$  (using Kröger-Vink notation).

To summarize, Figure 1 shows the defects and the chemical reaction taken into account in our model for multicomponent transport in zirconia during zirconium oxidation.



**Figure 1.** The model developed here studies multicomponent transport through the oxide considering chemical reaction between defects.

The concept of Conservative Ensemble, developed by J. Maier [1,2], leads to write down transport equation without a source term. The idea is to virtually set the defects into two groups, the group of oxygen related defects and the group of electron related defects. Doing so, the source terms is changed in a coupling term between the electrical fluxes and the ionic fluxes. These expressions fit into the framework of the thermodynamic of irreversible process. Furthermore, this formalism reduces the transport problem of the three particles in only one diffusion equation, introducing the chemical diffusion coefficient  $D^\delta$ , which is not constant with defects concentration.

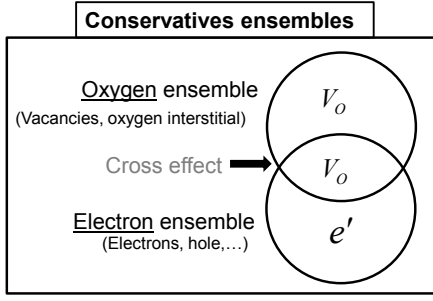
The notations used in this paper are defined in the appendix.

## 2. Master equation for zirconia oxidation

### 2.1 Theoretical background

#### Conservative ensemble

Two ensembles are defined (Figure 2), one for the oxygen related defects and another one for the electrons related defects [3].



**Figure 2.** Maier's Conservative ensemble [1]. The vacancy  $V_o$  leads to the cross effect between ensembles fluxes.

Each ensemble is conservative because the chemical reaction (equation 1, involving electron trapping by positive charged oxygen vacancies) does not change their concentration. This means that there is no source term for the transport equation of these ensembles.

$$V_o + e' = V_o \quad (1)$$

Each conservative ensemble characteristic can be written from defects one. For the oxygen related ensemble we have:

$$c_o^* = c_o^0 - c_{V_o} - c_{V_o} \quad (2)$$

$$J_o^* = -J_{V_o} - J_{V_o}$$

Equations 2 reflect the stoichiometry of oxide, concentration and fluxes of oxygen vacancies are constrained by these equations. For the electron related ensemble, we have:

$$c_e^* = c_{e'} + c_{V_o} \quad (3)$$

$$J_e^* = J_{e'} + J_{V_o}$$

Assuming the chemical reaction (equation 1) at equilibrium, the equality in chemical potential can be written as:

$$\eta_{V_o} = -\eta_o^* \quad (4)$$

$$\eta_{V_o} = -\eta_o^* + \eta_e^*$$

$$\eta_e = \eta_e^*$$

From the thermodynamics of irreversible processes, we have the flux of each defect:

$$J_i = s_i \nabla \eta_i \quad (5)$$

And then using the relation between chemical potential (equations 4) we finally write relations for ensemble fluxes:

$$J_o^* = -s_{oo}^* \nabla \eta_o^* - s_{oe}^* \nabla \eta_e^* \quad (6)$$

$$J_e^* = -s_{eo}^* \nabla \eta_o^* - s_{ee}^* \nabla \eta_e^*$$

With the following relations:

$$s_{oo}^* = s_{V_o} + s_{V_o}$$

$$s_{ee}^* = s_{e'} + s_{V_o} \quad (7)$$

$$s_{oe}^* = s_{e'o}^* = -s_{V_o}$$

## Oxygen transport

From equation 6 we can determine oxygen transport in zirconia using Wagner theory [4]. We assume electroneutrality in the oxide:

$$2J_o^* + J_e^* = 0 \quad (8)$$

From this relation one can write the total oxygen flux in the so called ambipolar form:

$$J_o = J_o^* = \frac{-\sigma_{amb}}{4q^2} \nabla \mu_o \quad (9)$$

Doing so, we define the ambipolar conductivity:

$$\sigma_{amb} = \frac{\sigma_{ee}^* \sigma_{oo}^* - \sigma_{eo}^* \sigma_{oe}^*}{\sigma_o} \quad (10)$$

Where each term is defined as:

$$\sigma_{oo}^* = 4q^2 s_{oo}^*$$

$$\sigma_{ee}^* = q^2 s_{ee}^* \quad (11)$$

$$\sigma_{oe}^* = -2q^2 s_{oe}^*$$

$$\sigma_o = \sigma_{oo}^* + \sigma_{ee}^* + 2\sigma_{oe}^*$$

We now define the chemical transport coefficient which leads to the global transport equation:

$$D^\delta = \frac{\sigma_{amb}}{4q^2} \left( \frac{d\mu_o}{dc_o^*} \right) \quad (12)$$

It highlights the ambipolar conductivity and the chemical capacitance effects. These terms contains all transport and chemical information. Their analytical forms are deduced from constraints applied on defects, as the electroneutrality, the stoichiometry and the chemical reaction. Finally we can write the global transport equation:

$$\frac{\partial c_o^*}{\partial t} = \nabla D^\delta \nabla c_o^* \quad (13)$$

The oxide thickness growth is determined from the oxygen flux defined at Metal/Oxide interface:

$$\frac{\partial e}{\partial t} = \frac{1}{c_{O,int}} J_{O,int} \quad (14)$$

## 2.2 Application for zirconium oxidation

### Chemical reaction constant

Noting K the constant of the chemical reaction (equation 1), it has the form:

$$K = N_C \exp\left(\frac{-E}{kT}\right) \quad (15)$$

With  $N_C = 2.8 \cdot 10^{22} \text{ cm}^{-3}$ , and E an energy term for which we will make parametrical study. The tests are done on two extreme cases. One for which  $V_O$  vacancies are fully ionized, the other for which vacancies  $V_O$  have trapped the electrons.

### Analytical form of the chemical diffusion coefficient

We first split the chemical capacity into an ionic term and an electronic one [5]:

$$\begin{aligned} \frac{\partial \mu_O}{\partial c_O^*} &= \frac{\partial(\mu_{O'} - 2\mu_{e^*})}{\partial c_O^*} \\ &= \frac{-\partial \mu_{V_O}}{\partial c_O^*} + 4 \frac{\partial \mu_{e^*}}{\partial c_e^*} \\ &= \frac{-\partial \mu_{V_O}}{\partial c_{V_O}} \frac{\partial c_{V_O}}{\partial c_O^*} + 4 \frac{\partial \mu_{e^*}}{\partial c_{e^*}} \frac{\partial c_{e^*}}{\partial c_e^*} \end{aligned} \quad (16)$$

Using the following relations and assuming ideal solution we can find analytical form of the differential terms in equation 16.

$$\begin{aligned} \sigma_i &= \frac{z_i^2 F^2 D_i c_i}{RT} \quad (\text{Stokes-Einstein}) \\ c_{V_O} + 2c_{V_O} - c_{e^*} &= 0 \quad (\text{Electroneutrality}) \\ c_O^* &= c_O^0 - c_{V_O} - c_{e^*} \quad (\text{Stoichiometry}) \\ K &= \frac{c_{V_O} c_{e^*}}{c_{V_O}} \quad (\text{Chemical reaction}) \end{aligned} \quad (17)$$

The chemical diffusion coefficient takes the form:

$$\begin{aligned} D^\delta &= \left( D_{V_O} + \frac{c_{e^*}}{K} D_{V_O} \right) t_{ee^*}^* I + \\ &\quad \left( D_{e^*} + \frac{c_{e^*}}{c_{e^*} + 2K} D_{V_O} \right) t_{OO}^* E + C \end{aligned} \quad (18)$$

Each term implied in this expression depends on the defects concentration, on the diffusions coefficients and on the chemical reaction constant.

### Master equations

We write the transport equation (equation 15) as a function of the electron concentration  $c_{e^*}$ :

$$\frac{A e_{ox} \partial c_{e^*}}{\partial t} = \nabla D^\delta \frac{A}{e_{ox}} \nabla c_{e^*} \quad (19)$$

with A given by:  $\partial c_O^* = A \partial c_{e^*}$ , i.e. :

$$A = - \left( \frac{2c_{e^*} + K}{c_{e^*} + 2K} - \frac{c_{e^*}^2 + c_{e^*} K}{(c_{e^*} + 2K)^2} \right) \quad (20)$$

The equation 19 is implemented in COMSOL Multiphysics using the PDE form in one dimension. The term  $e_{ox}$  stands for the oxide thickness. It appears in the transport equation (equation 19) because this equation is written in reduced coordinates for which we have:

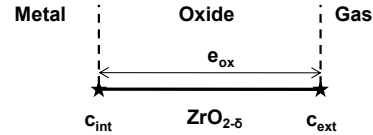
$$x_{reduced} = \frac{x_{real}}{e_{ox}} \quad (21)$$

$$\nabla|_{real} = \frac{1}{e_{ox}} \nabla|_{reduced}$$

Doing this leads us to have a constant geometry for the subdomain. The oxide thickness  $e_{ox}$  is solved from equation 14 implemented as weak form boundary term on the internal interface.

### Boundaries conditions

As illustrated in the Figure 3, we impose oxygen concentration at interfaces by fixing the oxygen nonstoichiometry  $\delta$ .



**Figure 3.** Oxygen concentration is fixed at metal/oxide interface and at oxide surface.

The electrons concentrations at boundaries are then deduced from  $\delta$  and from the following relations:

$$\begin{aligned} c_{V_o} + c_{V_o} &= \delta_{int/ext} \text{ (Stoichiometry)} \\ c_{V_o} + 2c_{V_o} - c_{e'} &= 0 \text{ (Electroneutrality)} \\ c_{V_o} \cdot c_{e'} &= K \cdot c_{V_o} \text{ (Chemical reaction)} \end{aligned} \quad (22)$$

By mean of some algebra:

$$c_{e'} = \frac{1}{2} \left( \delta_{int/ext} - K + \sqrt{\delta_{int/ext}^2 + 6\delta_{int/ext} \cdot K + K^2} \right) \quad (23)$$

Note that the initial oxide thickness is set to 10 nm.

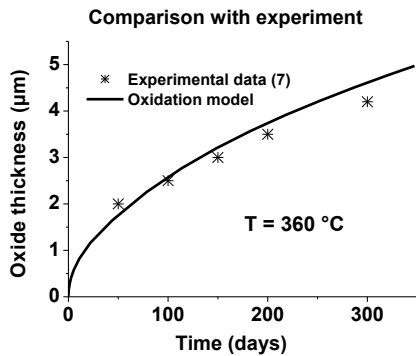
## 4. Results of the simulation

We study effect of several parameters implied in the oxidation model. Chemical diffusion and oxide growth evolution are deduced from the simulations.

### 4.1 Comparison with experiment

In the Figure 4 we compare oxide growth evolution from the model with experimental results taken from literature [7]. The oxygen vacancy diffusion coefficient evolution with temperature is taken from Debuigne [6] analysis, at 360°C the value is set to  $8 \cdot 10^{-18} \text{ m}^2 \cdot \text{s}^{-1}$ .

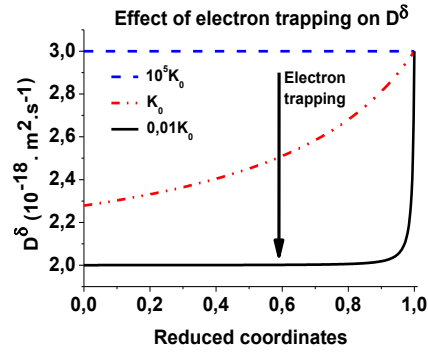
Simulation gives thickness in agreement with the experimental data. Furthermore the oxidation of zirconium at 288°C actually gives an oxide thickness around one micron for 350 days, which is the magnitude given by the simulation.



**Figure 4.** Comparison of the simulation results with data taken from literature [7]. Simulation gives oxide thickness in agreement with the experimental data.

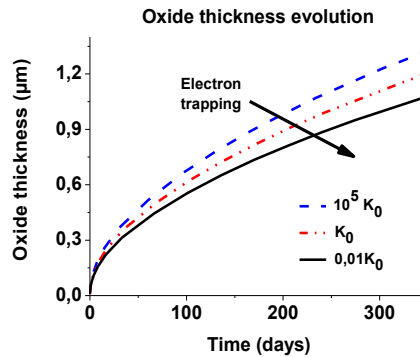
### 4.2 Effect of electrons trapping

By changing the value of the chemical constant  $K$  we change the dominant vacancy defect. Decreasing this value makes vacancies to trap electrons. The effect of electron trapping is shown on the Figure 5 and Figure 6.



**Figure 5.** The chemical diffusion coefficient  $D^\delta$  is not constant through the oxide. Electrons trapping decreases the chemical diffusion coefficient.

First, we can see that the chemical diffusion coefficient is not constant in the oxide, then that it decreases with electron trapping. This fact is consistent with J. Maier theory [8]. We then plot the oxide thickness as a function of electron trapping.



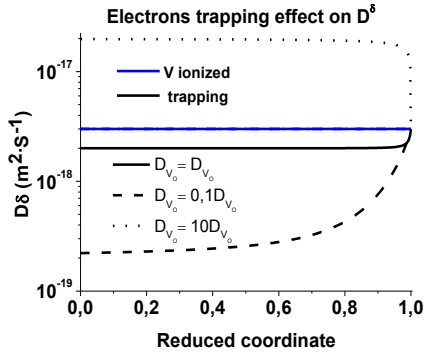
**Figure 6.** Electrons trapping effect on oxide growth.

Trapping electrons makes oxides lose 18 % of its thickness, which is not very significant. We next see this effect when vacancies diffusions coefficients are not the same for both charged defects.

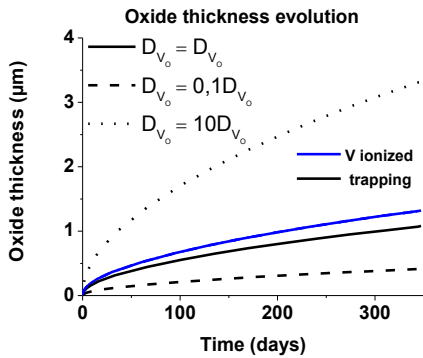
### 4.3 Effect of vacancies transport coefficient

When vacancies trap electrons, their diffusion coefficient can likely be modified. We now study this fact by parametrical studies on vacancies diffusion coefficient ratio. Results are plotted on Figure 7.

a)



b)



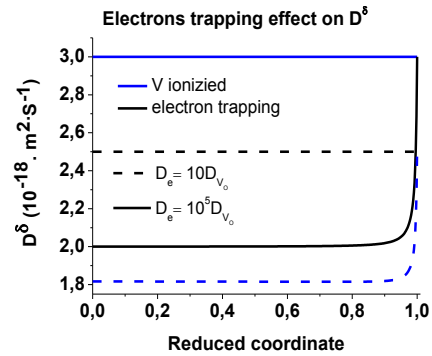
**Figure 7.** Effects of vacancies diffusion coefficient on oxide growth. Vacancies can have their diffusion coefficient modified by electrons trapping.

The results show that electrons trapping as well as vacancies diffusion coefficient have significant effects on oxidation growth kinetics. Transport coefficients still have more impact than the bulk chemical reaction. Here we need more insights on defects transport coefficients to know what effect electrons trapping can have on it.

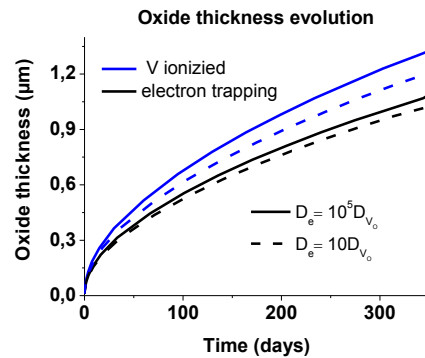
### 4.4 Effect of electrons diffusion coefficient

According to Wagner theory, oxygen diffusion assuming electroneutrality has an ambipolar form. In this context, the transport is limited by the lowest defect conductivity. We can check this point by changing electrons diffusion coefficient. Results are showed in Figure 8.

a)



b)

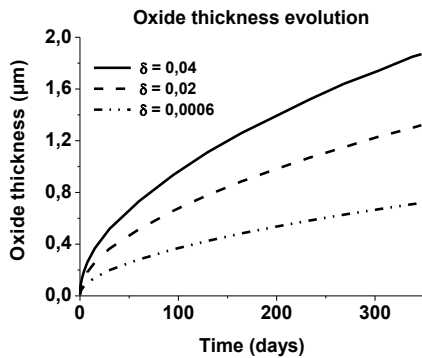


**Figure 8.** Effects of electrons diffusion coefficient on oxide growth. According to ambipolar transport the kinetics is limited by the lowest defect conductivity.

Increasing electrons transport coefficient has not so much effect on oxidation kinetics. However, it must be noted that this oxidation model works without polarization effect.

#### 4.5 Effect of nonstoichiometry

We now study the effect of nonstoichiometry at internal interface. We know that for zirconia, external interface is very close to stoichiometry. Changing this value, keeping close to stoichiometry, is not significant for oxidation kinetic. However, we don't know the exact value of nonstoichiometry at internal interface. Figure 9 shows parametrical study on this value.



**Figure 9.** Effect of internal nonstoichiometry. This value is related to the oxygen chemical potential at this interface. Increasing it increases the oxygen chemical potential gradient across the oxide.

Internal nonstoichiometry has an important effect on oxide growth. It corresponds to the chemical potential gradient across the oxide. The highest it is, the fastest the oxide growth.

#### 5. Concluding remarks

The model developed in this paper leads us to study zirconium oxidation from the transport of oxygen vacancies and electrons through zirconia and the bulk chemical reaction between these defects.

The model keys factors are the defects diffusions coefficients, the oxygen chemical potential gradient and the chemical reaction constant. All these parameters can be studied by this model. Magnitude of the oxide thickness deduced from the simulations is coherent with experimental data for zirconium oxidation. However, it is important to note that the model is not limited to study transport in zirconia. It can be used to study transport in all kind of materials which have an anionic transport behavior.

Finally, this model can be written in two dimension, using ALE moving mesh for the Metal/Oxide interface displacement. The two dimensions model enables to work on second phase particles on oxide. It just needs more insights on boundaries conditions between the inclusion and the matrix.

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## 7. Appendix

$c_O^*$	Oxygen ensemble concentration
$c_e^*$	Electron ensemble concentration
$J_O^*$	Oxygen ensemble flux
$J_e^*$	Electron ensemble flux
$c_O^0$	Zirconia perfect stoichiometry
$c_i$	Concentration of defect i
$J_i$	Flux of defect i
$\eta_O^*$	Oxygen ensemble electrochemical potential
$\eta_e^*$	Electron ensemble electrochemical potential
$\eta_i$	Electrochemical potential of defect i
$s_i$	Transport coefficient of defect i
$\mu_O$	Oxygen chemical potential
$\mu_i$	Chemical potential of defect i
$z_i$	Valence of defect i
$D_i$	Diffusion coefficient of defect i
$N_C$	Number of states in the conduction band
$\delta$	Zirconia nonstoichiometry
$q$	Elementary charge
$k$	Boltzmann constant
$T$	Temperature
$R$	Gas constant