Electrochimica Acta 55 (2010) 4451–4467

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Corrosion modelling of iron based alloy in nuclear waste repository

C. Bataillon[a,*], F. Bouchon[b,c], C. Chainais-Hillairet[b,c], C. Desgranges[a], E. Hoarau[e],
F. Martin[a], S. Perrin[a], M. Tupin[d], J. Talandier[e]

[a] CEA, DEN, DPC, SCCME, F-91191 Gif sur Yvette, France
[b] Clermont Université, Université Blaise Pascal, Laboratoire de Mathématiques, BP10448, F-63000 Clermont-Ferrand, France
[c] CNRS, UMR 6620, Laboratoire de Mathématiques, F-63177 Aubière, France
[d] CEA, DEN, DMN, SEMI, LM2E, F-91191 Gif sur Yvette, France
[e] ANDRA/DS, 92298 Châtenay-Malabry Cedex, France

ARTICLE INFO

Article history:
Received 14 October 2009
Received in revised form 25 February 2010
Accepted 27 February 2010
Available online 6 March 2010

Keywords:
PDM
Poisson
Oxide layer
Iron
Mott–Schottky

ABSTRACT

The Diffusion Poisson Coupled Model (DPCM) is presented to modelling the oxidation of a metal covered by an oxide layer. This model is similar to the Point Defect Model and the Mixed Conduction Model except for the potential profile which is not assumed but calculated in solving the Poisson equation. This modelling considers the motions of two moving interfaces linked through the ratio of Pilling–Bedworth. Their locations are unknowns of the model. Application to the case of iron in neutral or slightly basic solution is discussed. Then, DPCM has been first tested in a simplified situation where the locations of interfaces were fixed. In such a situation, DPCM is in agreement with Mott–Schottky model when iron concentration profile is homogeneous. When it is not homogeneous, deviation from Mott–Schottky model has been observed and is discussed. The influence of the outer and inner interfacial structures on the kinetics of electrochemical reactions is illustrated and discussed. Finally, simulations for the oxide layer growth are presented. The expected trends have been obtained. The steady-state thickness is a linear function of the applied potential and the steady-state current density is potential independent.

1. Introduction

The long-term behaviour of nuclear waste canisters in geological repository depends on (i) Thermo-Hydro-Mechanical (THM) behaviour of ground soils, (ii) metallic materials used to manufacture canisters and (iii) geochemical features of the ground in contact with the canisters. The disposal of nuclear waste canisters must be considered as a disturbance of the state of the clay fossil soil because (i) the canister is a source of heat but also because (ii) metallic canister corrodes. In clay soil, corrosion products like hydrogen and/or metallic cations induce geochemical transformations of the clay which induce changes in pH and redox potential of the surrounding clay of canisters which induce changes in corrosion conditions. In other words, the corrosion process and the geochemical transformations are linked. The 1000-years behaviour of metallic nuclear waste canisters could be predicted in linking corrosion, geochemical and THM models. The purpose of this paper is to propose an electrochemical model for this target.

This task seemed quite easy since at least two models have been proposed in the literature, i.e. the Point Defect Model [1–11] and the Mixed Conduction Model [12–16]. Both models assume that the metal is covered by a dense oxide layer. Mass and charges transports through the oxide layer are described as a field assisted diffusion of ionic defects or species. The PDM uses the Nernst–Planck equation whereas the MCM uses the Fromhold–Cook equation. Both models assume that the field strength in the layer is homogeneous and independent of the potential ($V = E - E_{SHE}$). The whole voltage drop V is distributed as two interfacial drops ($\Delta\phi_{m/f}$, $\Delta\phi_{f/s}$) and a bulk voltage εL:

$$V = \Delta\phi_{m/f} + \varepsilon L + \Delta\phi_{f/s} \quad (1)$$

where ε is the homogeneous field and L the layer thickness. To be consistent, both models introduce a parameter $\alpha_{f/s}$ called the outer interface polarizability which is defined as:

$$\Delta\phi_{f/s} = \alpha_{f/s} V + \Delta\phi^0_{f/s} \quad (2)$$

where $\alpha_{f/s}$ is constant and $\Delta\phi^0_{f/s}$ is a function of the external oxidizing conditions. For instance, $\Delta\phi^0_{f/s}$ is a linear function of pH [1]. In the case of the PDM, ε and $\alpha_{f/s}$ for iron have been estimated from the variation of the thickness L vs. potential E in borate buffer [1,17,18]. In the case of the MCM, ε and $\alpha_{f/s}$ have been estimated from Contact Electrical Impedance spectra [13].

Unfortunately, the fact that ε and $\alpha_{f/s}$ are free adjustable constant parameters implies that the application of the model could be

---

[*] Corresponding author. Tel.: +33 01 69 08 15 91; fax: +33 01 69 08 15 86.
E-mail address: christian.bataillon@cea.fr (C. Bataillon).

0013-4686/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2010.02.087

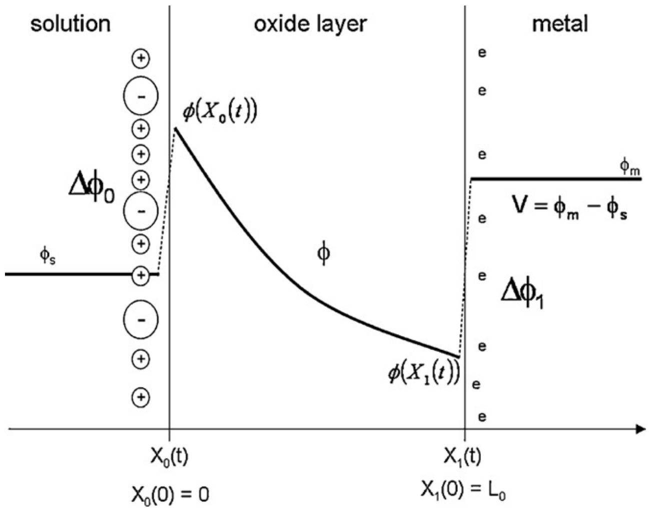

Fig. 1. Potential profile in the solution/oxide layer/metal system.

restricted to some bounded range of oxidizing conditions expressed in terms of potential range and chemical composition of the oxidizing solution. This is a paramount problem to link the corrosion model with other models which will describe the evolution of the oxidizing conditions. From a scientific point of view, ε and $\alpha_{f/s}$ have been introduced to describe the potential profile in the solution–oxide layer–metal system. This profile is basically the solution of the Poisson equation. The aim of this paper is to propose a model which takes explicitly into account the Poisson equation. This task is not so simple because the numerical resolution of the coupled Poisson and Fick equations is not trivial. Recently, Vankerberghen [19] has proposed a numerical resolution based on a finite-elements method. This resolution has been carried out with very special parameter values which lead to symmetric concentration profiles. Moreover, the net electroneutrality was restricted to the oxide layer which till lead to a symmetric field profile.

2. The basic equations of the modelling

Solid state transport of charge carriers in compact oxide layer is considered. These charge carriers could be point defects [20] or ions, electrons or holes. The whole system consists in a solution in contact with an oxide layer which covers a metal. Two interfaces bound the oxide layer. One is the inner interface which corresponds to the metal/oxide one. The other is the outer interface which corresponds to the oxide/solution interface. The metal is an electronic conductor. It could be charged either by accumulation or depletion of electrons. The solution is an ionic conductor. It could be charged either by accumulation of cations or anions. The oxide layer is a mixed electronic and ionic conductor (see Fig. 1).

Neither combination nor creation of charge carriers is considered inside the oxide layer. The charge carriers are created at one interface (inner or outer) and are consumed at the other (outer or inner). Inside the oxide layer, each charge carrier flux is assumed independent of the others because the physical mechanism for transport is generally typical of the kind of charge carrier (electronic transport in a conduction band, transport of ions by a vacancy mechanism, etc.).

2.1. The potential profile equations

The potential profile ϕ is given by the Poisson equation:

$$\nabla^2\phi = -\frac{F}{\chi\chi_0}\sum_i z_i c_i - \frac{\rho_{hl}}{\chi\chi_0} \tag{3}$$

where ∇^2 is the Laplacian. χ is the dielectric constant of the oxide, χ_0 the vacuum dielectric constant and F the Faraday constant. c_i is the concentration profile of the charge carrier i inside the layer, z_i its charge. The first term in the right hand side of (3) corresponds to the charge carriers. The second term ρ_{hl} corresponds to the net charge density of the host lattice (see Section 3.1.2). It has been assumed homogeneous.

As mentioned above, the solution and the metal could be charged. The charge of the solution σ_0 generates a field in the oxide layer. The same argument stands for the charge σ_1 carried by the metal. As a consequence, the interfacial charges generate a local field in the oxide layer in the vicinity of the corresponding interface (outer and inner). Theses local fields are given by Gauss laws:

$$\begin{cases} grad\ \phi[X_0(t)] = -\dfrac{\sigma_0[\Delta\phi_0]}{\chi\chi_0} \\ grad\ \phi[X_1(t)] = +\dfrac{\sigma_1[\Delta\phi_1]}{\chi\chi_0} \end{cases} \tag{4}$$

where $\Delta\phi_0$ and $\Delta\phi_1$ are respectively the voltage drop at the outer and the inner interfaces (see Fig. 1). Taking the potential of the solution ϕ_s as reference, the two boundary conditions are given by:

$$\begin{cases} \phi(X_0(t)) = \Delta\phi_0 \\ \phi(X_1(t)) = V - \Delta\phi_1 \end{cases} \tag{5}$$

where V is the applied potential between the metal and the solution (see Fig. 1).

It has been assumed that the interfacial charges of the solution σ_0 and of the metal σ_1 are described by:

$$\begin{cases} \sigma_0[\Delta\phi_0] = -\displaystyle\int_{\Delta\phi_0^{pzc}}^{\Delta\phi_0} \Gamma_0[\xi]\,d\xi \\ \sigma_1[\Delta\phi_1] = \displaystyle\int_{\Delta\phi_1^{pzc}}^{\Delta\phi_1} \Gamma_1[\xi]\,d\xi \end{cases} \tag{6}$$

The interfacial structure (outer and inner) has been described by a differential capacitance (Γ_0 and Γ_1) and a corresponding voltage of zero charge ($\Delta\phi_0^{pzc}$ and $\Delta\phi_1^{pzc}$).

In the Diffusion Poisson Coupled Model (DPCM), the first integration of the Poisson equation (3) over the whole layer (from $X_0(t)$ to $X_1(t)$, see Fig. 1) gives:

$$grad\ \phi[X_1(t)] - grad\ \phi[X_0(t)] = -\frac{F}{\chi\chi_0}\sum_i z_i \int_{X_0(t)}^{X_1(t)} c_i[x]\,dx - \frac{\rho_{hl}}{\chi\chi_0}(X_1(t) - X_0(t)) \tag{7}$$

Introducing the Gauss laws (4), the net electroneutrality equation is obtained:

$$\sigma_0[\Delta\phi_0] + F\sum_i z_i \int_{X_0(t)}^{X_1(t)} c_i[x]\,dx + \rho_{hl}(X_1(t) - X_0(t)) + \sigma_1[\Delta\phi_1] = 0 \tag{8}$$

In the simplest case where the oxide layer does not contain any charge carrier ($c_i \equiv 0$) and is stoichiometric ($\rho_{hl} = 0$), the net electroneutrality of the whole system implies that $\sigma_0 = -\sigma_1$. So, the two local fields defined by (4) are equal. This limiting case corresponds to those of a pure capacitance.

2.2. The moving boundaries equations

It has been assumed that the outer and the inner interfaces could move with time. The origin of the space axis is the location of the outer interface $X_0(0)$ at the initial time ($t = 0$). The initial thickness L_0 of the oxide layer defines the initial location of the inner interface $X_1(0) = L_0$ (see Fig. 1).