

Steady state analysis of thin oxide barrier layers formed in neutral and weakly alkaline solutions.

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Thin passive films are investigated in neutral and weakly alkaline pH solutions under steady-state conditions. The oxide films are considered highly defective with defects of the following types: oxygen vacancies, metal interstitials and metal vacancies (both with one or more oxidation states, depending on the oxide). Starting with the reactions model proposed by the "Point Defect Model" (PDM) (1) we propose a mathematical model that describes the transport of species through the oxide from the interface with the electrolyte to the interface with the metal (2).

The main objectives of this study are: a) an agreement between the simulation results and the experimental data available on this topic, b) to provide detailed information regarding dopants distribution in the barrier layer, potential drops across the interfaces and the bulk oxide, electric field levels and influence of the pH on the general properties of the oxide films and c) to discuss the parameter values that were obtained from the fitting with values encountered in literature (diffusion coefficients, dielectric constant of the oxide etc.)

A system comprising of an electrode on which a thin barrier layer is already formed and in contact with an electrolyte solution is considered (see figure 1). The dilute solution theory of Newman (3) is proposed to model the transport of species through the oxide and in the electrolyte solution (one mass balance equation, eq. 1, for each species), coupled with the Poisson equation (eq. 2) to account for the potential distribution in the oxide (2). In the electrolyte solution the Poisson equation is resumed to the electro-neutrality condition.

$$0 = -\vec{\nabla} N_i \quad [1]$$

$$\varepsilon \cdot \vec{\nabla}^2 U + F \cdot \sum_{i=0}^I z_i c_i = 0 \quad [2]$$

The coupled set of differential equations (one set for the oxide and one set for the electrolyte solution) is solved using the Finite Element Method (FEM). In order to obtain accurate and grid independent solutions, the computational grid of the oxide contains very small elements with sizes of 10^{-12} – 10^{-11} m. Non-uniform grids were chosen for the electrolyte solution. The total length of the system is $d = 5 \times 10^{-6}$ m (for all simulations). Figure 1 shows the electrochemistry at the interfaces and the directions in which species are transported through the oxide. The reactions taking place at the interfaces are potential dependent and are of Tafel type (4):

$$v_i = k_i^0 \exp\left(\frac{\alpha_i q_{ex} F}{RT} \eta(x)\right) \prod_j c_j(x) \quad [3]$$

k_i^0, α_i, q_{ex} are kinetic parameters for the considered reaction, F is the Faraday constant, R the ideal gas constant, T the temperature and $\eta(x)$ is the overpotential at the particular interface where the reaction takes place. A virtual counter electrode was taken at

$x = d$, where the concentrations of the species involved are also set to their bulk values and the potential in the electrolyte is initialized with 0.

The mathematical model is applied on the spinel iron oxide and is fitted against experimental data (5). The whole procedure takes place in the passive range of potentials corresponding to the iron oxide in neutral pH solutions. The simulation results show good agreement with experimental data and are able to provide information that is not readily available from an experimental point of view.

After a set of results is obtained which is in agreement with experimental data, we will investigate the influence of higher or lower diffusion of species through the oxide, on the overall steady-state properties of the oxide. Thus we will try to account for the variety of diffusion coefficients values which are seen throughout literature (6). Also other parameters that might have an influence on the general behavior of the oxide film are investigated.

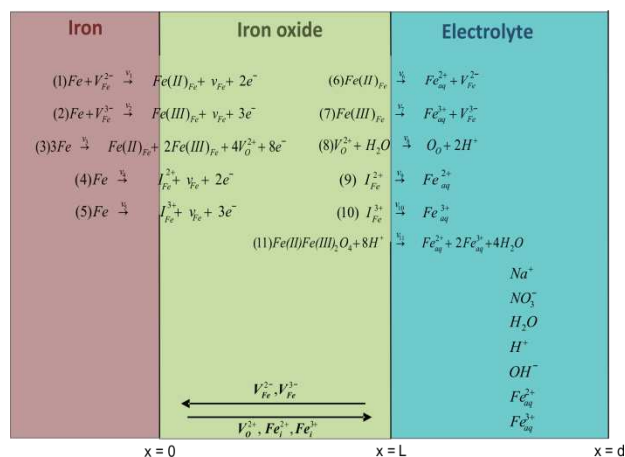


Fig. 1 Application of the PDM reactions model on the spinel iron oxide in contact with an electrolyte solution

References

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