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A modelling approach on the impact of an oxide layer on the hydrogen permeation through iron membranes in the Devanathan-Stachurski cell

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ABSTRACT

The diffusion and trapping of hydrogen in iron alloys is commonly studied using the Devanathan-Stachurski cell. In this cell, the hydrogen flux through a metal membrane is studied. At the exit side of the membrane, an oxide layer is commonly developed and stabilized as a consequence of the anodic polarization imposed. The process of hydrogen diffusion through the oxide layer and its consecutive oxidation is not fully understood yet. In this paper, we propose a modelling approach that provides additional insights in this process. In particular, we highlight the impact that the presence of the oxide layer can have on the overall hydrogen transport throughout the metal membrane. Moreover, we highlight the complexity of this mechanism and discuss the possible reactions taking place in and at this interface. As a conclusion a possible alternative process to explain the findings is proposed.

1. Introduction

The Devanathan-Stachurski cell is the most widely used electrochemical technique to study hydrogen diffusion and trapping in iron alloys [1]. This cell is a flexible set-up commonly used to determine the diffusion coefficient and the trapping effects of hydrogen in steels [2,3]. In this cell, an iron-alloy membrane is used to study the hydrogen transport process: at one side of the membrane, a negative potential is applied to force hydrogen adsorption on the surface of the sample. Part of the adsorbed hydrogen atoms will then ingress the sample and diffuse into the sample bulk as absorbed atoms. For this reason, this side of the membrane is commonly named entry side. The absorbed hydrogen diffuses through the steel membrane and arrives to the other surface, commonly referred to as exit side. On this surface, hydrogen atoms are oxidized due to an imposed anodic potential. An anodic current is recorded, which is dependent on the hydrogen flux reaching the exit side.

Regardless of the methodology and the scope for which this cell is used, a very alkaline environment is commonly employed as exit electrolyte. In these electrochemical conditions, the anodic polarization imposed at the exit side induces the formation of an oxide layer on the steel membrane [4]. To this regard, questions on the interaction between hydrogen and the oxide layer formed and on the hydrogen desorption mechanism at the exit surface are still to be answered. For this reason, many authors consider the results obtained with this methodology to be practically unsuitable [5–7]. To tackle this problem, researchers apply Pd-coatings on the top of either the entry and/or the exit surface. This methodology was commonly employed in earlier research, performed before the '90s. Indeed, some of the most relevant works on hydrogen diffusion in steel were obtained with this methodology [8,9]. Nevertheless, this procedure is less and less employed nowadays, raising questions on the reliability of the results obtained.

Even though a complete oxidation of hydrogen on Pd was proven under certain conditions [10], the procedure of applying the Pd coating to the surfaces is almost never described in an article and the exact characteristics of the Pd-Fe interface are not known, however it is known that the surface state has a significant influence on the kinetics of hydrogen recombination reactions. Usually, two methodologies are employed for the Pd coating procedure:

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chemical/electrochemical deposition, or sputter deposition in ultra-high vacuum (UHV). In the first case, an oxide layer can be present on the surface of the iron alloy prior to palladium deposition. Incomplete elimination of this layer leads to the presence of a trap in the interface [11]. Moreover, the introduction of hydrogen during the Pd electrodeposition is also possible. In the second case, the pre-existing oxide layer is removed by the ion bombardment, which in turn can create defects to the surface structure. This factor raises doubts on whether this procedure induces further trapping effects in the system and on the correctness of the experimental results obtained. Indeed, *Brass* et al. [12] conducted specific analysis on the state of the Fe-Pd interface after hydrogen permeation tests, showing significant trapping of hydrogen in the Fe-Pd interface in some cases, suggesting that extreme care should be taken when interpreting permeation results obtained on Pd-coated iron alloys. The fact that authors are commonly not describing the Pd-coating procedure was also stressed by *Driver* [11]. In his work, he insists on the wide variety of contradictions in the existing data, attributing the problem to different coating methods employed by the researchers, which lead to imperfect, porous and excessively thin Pd layers. *Driver* also proposes an electrochemical procedure to obtain pore-free, 1.5–2.0 μm thick coatings. Other authors [13] opine that electrodeposition of Pd could introduce hydrogen to the metal sample and the inevitable disbonding of the Pd layer during the hydrogen permeation process. Nevertheless, it must be mentioned that, if the Pd coating procedure is achieved with a correct methodology, reasonably traps at the Fe-Pd interface will be negligible as they are quickly filled. Still, given the significant impact the nature of the procedure used can have on experimental results, it is important to note that in future papers authors at least specify the experimental methodology and the technique employed.

Specific research on the difference between the use of Pd-coated and Pd-free surfaces is hard to find. *Bruzzoni* et al. [6] conducted specific investigations on this subject on steel membranes employing thin samples, showing reduced permeability and delayed diffusion with Pd-free surfaces (Fig. 1). These changes are related to the different condition of the exit surface, all other parameters being the identical. *Manolatos* et al. [14] found similar results, remarking the presence of hydrogen bubbles at the exit side, which can only be formed due to chemical hydrogen recombination at this surface. Bubbles at the exit side where also observed elsewhere [15]. This observation highlights the necessity of applying a Pd layer on the exit side surface.

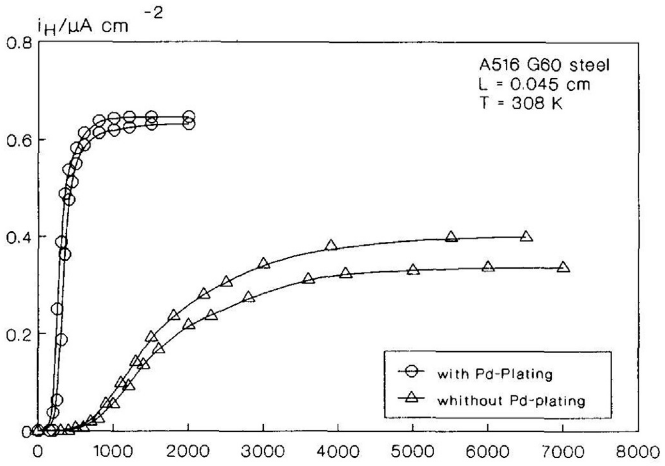

Fig. 1. Experimental results proposed by Bruzzoni et al. [6]: comparison between Pd-coated and Pd-free surfaces.

Although the experimental results obtained in these conditions are criticized in the papers referred to, there is no doubt regarding the fact that the current recorded is representing only the hydrogen flux [16]. Moreover, both *Bruzzoni* et al. [6] and *Manolatos* et al. [7] demonstrated the possibility to obtain reproducible results. This fact, combined with the work of *Casanova* et al. [17], who proved the neutrality of the presence of an oxide layer to the hydrogen transport process, and the verified unaltered hydrogen flux in complex systems involving thin iron foils (and its oxide layer) [18], shows that obtaining reliable results with Pd-free surfaces in valuable conditions may be possible.

Pd-coated surfaces are less and less used in nowadays research [4,16,19,20] and are commonly replaced by a passivation procedure of the exit surface [21,22]. According to this method, the exit surface is passivated for several hours to stabilize the oxide layer [4,22]. Afterwards, the hydrogen permeation is started and a current related to the hydrogen oxidation reaction is recorded at the exit side. With the presence of an oxide layer at the exit side, hydrogen atoms are forced to travel through an additional system before getting in contact with the anodic electrolyte. Due to this effect, the hydrogen concentration at the exit side is not zero, as the barrier effect produced by the presence of the oxide layer is remarkable in respect to the hydrogen oxidation at the exit side [7,9]. This is a very sensitive point as many of the equations used to calculate diffusion coefficients in metals are derived from a constant zero-concentration assumption [23].

Even though there is no general agreement on the mechanism of hydrogen diffusion in an iron oxide layer, common opinion is that hydrogen diffuses in the atomic form. Due to the remarkably low diffusion coefficient of hydrogen atoms in the oxide, the presence of an oxide layer at the exit side was commonly reported to act as an important barrier to the hydrogen flow [6,24,25], slowing down this process. Moreover, it was found that the properties of the oxide layer change in presence of hydrogen [26,27]. This point is fundamental for the analysis of permeation curves in iron alloys. Moreover, many researchers investigated in depth the effect of the oxide layer on the hydrogen diffusion process [9,16,28,29], agreeing on the fact that hydrogen is diffusing in the lattice sites of the oxide compound in its proton form, or at least with a partial charge. In this case, the hydrogen diffusion would be prompted by the presence of an electric field through the oxide layer [16], resulting from the anodic polarization imposed, possibly not having a considerable barrier effect at the imposition of a sufficiently positive potential.

The hydrogen diffusion process through the oxide layer and consecutive desorption process is not yet fully understood [6,28,29]. To tackle this problem, we decided to employ numerical modelling as a tool to study the effects of the presence of an oxide film at the detection side of the sample in a permeation cell. Possible mechanisms taking place at the exit side of the Devanathan-Stachurski cell will also be discussed. In our previous work [30,31], we developed and validated a model able to successfully reproduce all stages of the hydrogen transport process in the permeation cell, including the adsorption, absorption, diffusion, trapping and desorption steps.

In this paper, we will propose an improvement of the earlier proposed model to demonstrate the impact of the presence of an oxide layer at the exit side. With the employment of the Finite Element method (FEM), we are able to build a numerical, time-dependent model to simulate the hydrogen transport process at all its stages from the entry to the exit of the membrane, as well as to track the variation of hydrogen concentration and flux in time. A FEM based model is the perfect tool to investigate the processes taking place in each subsystem of the Devanathan-Stachurski cell.