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The present work was carried out at the Institute of Chemical Technologies and Analytics of the Technical University of Vienna.

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List of symbols used

| L | [cm] | Thickness |
|-------------------------|------------------------|---|
| D | [cm ² /s] | Effective diffusion constant |
| T _{lag} | [s] | Time lag |
| t _b | [s] | Breakthrough time |
| c 0 | [mol/cm ³] | Surface concentration of hydrogen |
| j∞ | [A/ cm ²] | The stationary current density |
| F | [C/mol] | Faraday constant |
| j | [µA/cm²] | Current density |
| t | [s] | Time |
| S | [mol/cm ²] | Total hydrogen mole per square centimeter |

List of abbreviations used

| HE | Hydrogen embrittlement |
|------|--|
| HER | Hydrogen evolution reaction |
| D&S | Devanathan & Stachurski |
| HIC | Hydrogen induced cracking |
| SCC | Stress corrosion cracking |
| HAR | Hydrogen absorption reaction |
| HEDE | Hydrogen enhanced decohesion embrittlement |
| HELP | Hydrogen enhanced localized plasticity |
| WEC | White etching cracks |
| WEA | White etching area |
| ZDDP | Zinc dialkyldithiophosphates |

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Abstract

The main objective of the present diploma thesis was the research support in the analysis of the influence of electric field effects on oils in contact with steel surfaces with an emphasis on hydrogen generation and permeation in steel. The main focus of the thesis was the optimization of the test method concerning reproducibility. For this purpose, two different lubricants BO318 and PFPE were tested by measuring the hydrogen permeation flow through a steel membrane using electrochemical Devanathan and Stachurski technique. A reproducibility of the results was achieved by changing the pretreatment of the steel samples and by drying the filter paper impregnated with the lubricants. By comparing the results of the different test series of the PFPE oil, it was noticed that the measured current at the end of the tests was in the same value range. During experiments it was revealed that secondary hydrogen is constantly generated on the counter electrode. Thus, in order to prevent the diffusion of the hydrogen from the cathode to the anode, and thus to avoid its contribution to the hydrogen generation and permeation occurring from the steel-oil contact, the cell was constantly purged with nitrogen. This approach proved to be successful, allowing the true protonic current being measured in the conducted experiments.

Zusammenfassung

Das Hauptziel der vorliegenden Diplomarbeit war die Forschungsunterstützung bei der Analyse des Einflusses von elektrischen Feldeffekten auf Öle in Kontakt mit Stahloberflächen mit Schwerpunkt auf Wasserstofferzeugung und Permeation in Stahl. Das Hauptaugenmerk der Arbeit lag auf der Optimierung des Prüfverfahrens hinsichtlich der Reproduzierbarkeit. Zu diesem Zweck wurden zwei verschiedene Schmierstoffe BO318 und PFPE getestet, indem der Wasserstoffpermeationsstrom durch eine Stahlmembran mittels der elektrochemischen Devanathan und Stachurski Technik gemessen wurde. Eine Reproduzierbarkeit der Ergebnisse wurde durch die Veränderung der Vorbehandlung der Stahlproben und durch das Trocknen des Filterpapiers, welches mit den Schmierstoffen imprägniert wurde, erreicht. Durch Vergleichen der Ergebnisse der verschiedenen Testreihen des PFPE Öls, fiel auf, dass der gemesse Strom am Ende der Versuche sich stets im selben Wertebereich befunden hat. Bei Experimenten zeigte sich, dass an der Gegenelektrode ständig ein sekundärer Wasserstoff erzeugt wird. Um eine Rückdiffusion des Wasserstoffs von der Kathode zur Anode und damit seinen Beitrag zur Wasserstofferzeugung und Permeation durch den Stahl-Öl-Kontakt zu verhindern, wurde die Zelle daher ständig mit Stickstoff gespült. Dieser Ansatz erwies sich als erfolgreich, so dass in den durchgeführten Experimenten der wahre Protonenstrom gemessen werden konnte.

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1. Introduction

Atomic hydrogen is one of the most harmful sources for the structural stability of metals and their alloys due to its small size and the associated possibility of spreading in the material. Hydrogen can penetrate into metals from various sources, e.g. acidic pickling, electroplating, corrosion, cathodic protection, and welding. A special case is the contact of the steel with an environment containing hydrogen sulfide. The resulting corrosion process due to the contact generates atomic hydrogen. This hydrogen is absorbed by the metal, whereby some part is stored in the defects and grain boundaries leading to the phenomenon known as hydrogen embrittlement (HE). The latter is considered as a major problem in the petrochemical industry [1,2].

An increase in the hydrogen concentration in the steel from 0.03 mass-ppm to 1.2 mass-ppm, shortens the component fatigue life more than one order of magnitude [1]. Whereby, steels with a tensile strength between 800-1000 MPa or higher are most affected by the HE phenomena [2], [3]. Overall, HE results in safety problems with the steel components and poor performance e.g. in oil industries, motors, medical implants, and constructions [4]–[12].

The permeability of hydrogen is mostly regulated by the intrinsic properties of the metal. The number and kind of defects, as well as the adsorption ability of the surface are other important factors to consider. The hydrogen evolution reaction (HER), which in the first place provides the hydrogen for the diffusion, depends on the environment characteristics such as the pH value and the composition of the solution, especially on the presence of additives in it, which can trigger or perhaps prevent the entry of the hydrogen.

For a better understanding of the hydrogen dynamics in metals and the metal permeability towards hydrogen, a device capable to detect hydrogen concentration in the ppm range is of crucial importance. As it was mentioned above, even tiny changes in the hydrogen concentration lead to dramatic outcomes for the metal stability.

Several analytical methods exist for the detection of hydrogen e.g. thermal desorption spectroscopy or nuclear reaction analysis as well as the electrochemical permeation technique developed by Devanathan & Stachurski (D&S) [13]–[18]. In this work, the electrochemical approach by D&S was utilized based on the fact, that this method is pretty fast and delivers precise information because of its high sensitivity. Furthermore, it provides us with the

determination of e.g. the diffusion constant of hydrogen or the surface concentration of hydrogen [13], [19].

Another great advantage of the electrochemical approach is the possibility to analyze local hydrogen evolution at the membrane in the diffusion measurements. By changing the solution, the current density, or the polarization potential, one can obtain a desired hydrogen evolution. Furthermore, expensive equipment for high-pressure hydrogen gas charging is superfluous.

The main objective of this work was the research support in analyzing the influence of electric field effects on oils in contact with steel surfaces with a focus on hydrogen generation and permeation into the bulk steel. The proposed method was validated by utilizing the hydrogen permeation technique of D&S for the prediction of hydrogen-related damages of steel in contact with technologically relevant lubricants. This master thesis mainly focus on the optimization of the testing procedure regarding its reproducibility. For this purpose, two structurally different lubricants were tested by measuring the hydrogen permeation current through a steel membrane.

2. Theoretical principles

2.1. Causes for hydrogen embrittlement

The first cases of Hydrogen Induced Cracking (HIC) were reported at the end of the 19th century [20], [21]. Despite intensive research works in this field, there is still a lack of a generally valid theory, which considers various changes in the mechanical behavior of the material caused by hydrogen atoms [22]–[24]. The currently prevailing opinion is that the damage observed in different materials is due to different hydrogen accumulation mechanisms [25].

A prerequisite for the occurrence of environment-related material damage caused by hydrogen is an interaction of hydrogen source, hydrogen entry (absorption), and hydrogen transport to the site of embrittlement in the material itself. In the case of Stress Corrosion Cracking (SCC), a further requirement is the presence of a mechanical force. A large number of possible combinations between material, mechanical stress, and chemical action are possible. Although extensive results on the problem of stress corrosion cracking are available in the literature, these cannot be readily used in individual cases. Especially, at the boundary layer to aqueous media, there are difficulties in investigating the responsible reactions and their effect on the generation and subsequent absorption of hydrogen. The fact that metallic materials are mostly made from alloys, makes possible a large number surface layer reactions at the boundary layer for each material/environment combination. Besides, in the case of cracked components, metals are usually provided with a protective oxide layer which, if the crack is prolonged, is destroyed and thus promotes metal dissolution. A further effect is that mechanical deformation produces fresh metal surfaces which are assumed to reduce the activation energy of deposition and thus promote hydrogen absorption. It must also be kept in mind that the chemical composition of the corrosion medium (pH, salt content) in a crack or gap may differ from that outside the crack [26].



Figure 1 Schematic representation of some possible influencing variables in a material/medium pair on the different phases during hydrogen induced crack propagation

(HER = Hydrogen Evolution Reaction, HAR = Hydrogen Absorption Reaction)

Figure 1 shows a combination of parameters in a hydrogen-producing medium system, whose influence on partial steps of hydrogen embrittlement in experiments could be proven. As possible sources for external hydrogen in the technology are in addition to gaseous hydrogen, the application of protective potentials, welding under inert gas, the electroplating of metal surfaces or cleaning in acid baths [27]–[29]. Any media containing hydrogen based gases, particularly H₂S, poses a risk to the service life of its components, since the gases can greatly increase the hydrogen ingress at the boundary layer of the material [30], [31]. Thus hydrogen absorption is the only one from the three above-mentioned boundary layer phenomena Substep, which depends both on the medium and one the material used.

Ultimately, hydrogen diffusion highly plasticizes the material in the vicinity of the crack as a result of increased local stresses, and thus determines whether a component of that material will fail within a given period. The decisive factor in hydrogen transport in ferrous materials is their lattice structure. Both the diffusion rate and the solubility of hydrogen in

the material depends essentially on the existence of so-called hydrogen traps, such as dislocations, grain boundaries, vacancies, impurity atoms or microcracks. The total number of these traps depends on the stress and strain state, or of the deformation mechanism involved [32], [33].

2.2. Hydrogen absorption through cathodic polarization

When a metallic object comes in contact with hydrogen, the latter can penetrate into the metal under certain conditions. The entry can come either from the gas phase or through direct hydrogen deposition on the metal surface. Gaseous Hydrogen (H₂), however, is not readily absorbed by the iron atoms at room temperature because its dissociation energy (436.22 kJ/mol), is not compensated by the energy released from the adsorption and dissolution process (endothermic solution) [34]. The presence of atomic hydrogen at the gas-metal interface, on the other hand, spontaneously leads to a significant hydrogen absorption to bulk of iron and steels [35].

The reduction of protons on the surface of a cathodically polarized electrode produces hydrogen according to the following equation:

$$2H^+ + 2e^- \to 2H_{ad} \tag{2.2a}$$

$$2H_2O + 2e^- \to 2H_{ad} + 2OH^-$$
 (2.2b)

This reaction is important for corrosion protection, since it prevents or can at least slow down the galvanic dissolution of iron and steels by applying an electrical potential. Provided that the applied potential is greater than a certain threshold value, the reactions defined by eqs. (**2.2**a) and (**2.2b**) are initiated and lead to the production of intermediate atomic hydrogen. Concerning the electrode kinetics, two different reaction mechanisms are discussed in the literature, which can be considered as experimentally proven [36].

2.2.1. Volmer-Tafel-Mechanism



Figure 2 Reaction mechanism for the hydrogen absorption from an electrolyte solution according the Volmer -Tafel reaction

If a metal is present in an aqueous electrolyte, all positive ions occuring in the solution as hydronium ions (H_3O^+) under equilibrium conditions will react with the conduction band electrons of the metal, and, after several consecutive steps inert H₂ molecules will be formed. In the first step, H⁺ ions migrate from the solution to the metal surface where they are discharged to an adsorbed hydrogen atom according to the Volmer reaction (2.2c). In the next step, according to the Tafel reaction, two absorbed hydrogen atoms can recombine to form a molecular hydrogen (2.2d) [37].

$$H^+ + e^- + Fe \rightarrow Fe - H_{ad}$$
 (Volmer-Reaction) (2.2c)

$$Fe-H_{ad} + Fe-H_{ad} \rightarrow H_2 + 2Fe$$
 (Tafel-Reaktion) (2.2d)

In alkaline solution the Volmer-Reaction is usually modified according to the following equation,

$$H_2O + e^- + Fe \to Fe - H_{ad} + OH^-$$
(2.2e)

The atomic hydrogen in the equations (2.2c) and (2.2e) is in a chemisorbed state, i.e, there is a covalent bond between the hydrogen and the iron atom on the metal surface.

2.2.2. Volmer-Heyrowsky-Mechanism



Figure 3 Reaction mechanism for the hydrogen absorption from an electrolyte solution according the Volemer - Heyrovsky reaction

The Volmer-Reaction of the hydrogen discharge can be also followed by a sequence of reactions first proposed by Heyrovsky and named after him [37].

 $H^{++e^{-+Fe \rightarrow Fe-H_{ad}}}$ (Volmer-Reaction) $H^{++Fe-H_{ad}+e^{-\rightarrow H_2+Fe}}$ (Heyrovsky-Reaction) (2.2f)

The Heyrowsky reaction involves the discharge of a solvated proton (hydronium) at the hydrogen atom, which was previously adsorbed on the metal surface. This reaction takes place in the cathodic current direction and results in the formation of molecular hydrogen which then desorbs from the cathode. In alkaline solutions, the Volmer-Reaction (2.2e) is followed by the reduction of water molecules. In this case the reaction scheme is:

$$H_2O + Fe - H_{ad} + e^- \rightarrow H_2 + Fe + OH^-$$
(2.2g)

It is not well understood yet which of the two hydrogen deposition mechanisms dominates for iron and its alloys in alkaline solutions. In the case where a metal has the ability to absorb hydrogen (this case is elaborated in **section 2.3.3),** hydrogen formation in the solution and its absorption occur simultaneously. Experimental data of the absorption rate, e.g. in permeation measurements, allows to draw conclusions about the leading mechanism of hydrogen generation.

2.2.3. Absorption mechanism by the metal surface



Figure 4 Reaction mechanism for the hydrogen absorption from an electrolyte solution according the hydrogen absorption reaction

Because of their small size, hydrogen atoms are capable of dissolving in the bulk metal. Bockris proposed a new model for the hydrogen absorption by the metal surface (Hydrogen Absorption Reaction, HAR) [31]. The main idea is based on the assumption that hydrogen chemisorbed on the surface by the Volmer-Reaction will be rather absorbed than recombined,

$$H^+ + e^- + Fe \rightarrow Fe - H_{ad}$$

 $Fe - H_{ad} \rightarrow H_{ab} + Fe$ (HAR) (2.2h)

As a result, the absorption of the chemisorbed hydrogen on the metal surface can be regarded as a competitive reaction to the Tafel and Heyrovsky reactions.

The reaction rate in eq. (2.2h) is proportional to the degree of coverage of the surface with atomic hydrogen [38]. Further regarded as a flux of free atoms, the relationship for hydrogen absorption becomes

$$J = k_{abs}\theta_H - k_{des}c_0 \tag{2.2i}$$

where θ_H is the degree of coverage of the metal surface, c_0 is the hydrogen concentration in the vicinity of the metal surface, k_{ads} and k_{des} are the rate constants of the absorption or desorption steps. In comparison to other metals such as palladium, iron has relatively low degree of coverage ($\theta_H = 0,01$) due to the rapid recombination reaction (Eq. 2.2c and 2.2e). Consequently, only a small part of the hydrogen produced is absorbed by the metal. With so called promoters such as H₂S, HCN, As₂O₃, CO or CO₂, hydrogen absorption can be sufficiently increased [19], [30], [39]. Because the recombination of the adsorbed hydrogen on the surface is made more difficult, thus increasing the probability that reaction (2.2h) can take place [40]. The disadvantage of such increase in the hydrogen concentration on the inlet side, especially in low-alloy steels, is the formation of microcracks in the metal, which negatively influence the subsequent hydrogen diffusion through the additionally created defects [41].

2.3. Hydrogen transport in iron and steel

2.3.1. Solubility of hydrogen in the metal

The interstitially dissolved hydrogen is extremely mobile and is accumulated in interstitial sites in the metal until saturation is reached [42]. In transition metals hydrogen donors its electron to the lattice gas and is present as a so-called shielded proton [43]. According to Oriani, the concentration of hydrogen atoms stored on interstitials C_L is given by the equation

$$C_L = \theta_L N_L \tag{2.3a}$$

where θ_L is the degree of coverage and N_L the concentration of the intersitials [44]. Body centered cubic α -iron has 12 tetrahedral and 6 octahedral open spaces, of which one can be occupied by hydrogen atoms. If it is assumed that hydrogen atoms occupy only the open spaces in the tetrahedra at room temperature, N_L amounts in pure α -iron 5.1 * $10^{23}/m^{-3}$ [45].

Generally, metallic materials have defects in their atomic lattice structure, e.g. due to manufacturing process. These can be voids, grain boundaries, or dislocations (**Figure 5**), which, due to the resulting local distortions of the atomic lattice, promote the ingress of hydrogen in the metal. This effect is known as hydrogen trapping in solid structures [46]–[48]. These traps are usually divided into reversible (from flat to medium traps) and irreversible (from medium

to deep traps) trap classes according to their hydrogen binding energy E. The latter corresponds to the energy difference between the dissolved state in the bulk and that in the trap. Reversible traps with energies E<30kJ/mol per H include areas in the material that have a distorted lattice due to the application of an external mechanical load or due to their own elastic fields around the dislocations. In this area of increased stress, atomic hydrogen atoms can attach and dwell in. If, however, the external mechanical load is reduced or the equilibrium ratio of the atomic hydrogen is changed, hydrogen atoms can detach from adherents and continue to diffuse. Thus, reversible traps can be regarded as temporary hydrogen sources. In irreversible traps with energies E>50kJ/mol per H, the bonding energy to hydrogen is so high that the attached atomic hydrogen does not dissolve even if the mechanical stress or the equilibrium ratio is changed. These traps act as eternal sinks. If a material has a high proportion of internal phase boundaries, the hydrogen is increasingly bound in irreversible traps and diffusion is delayed [56], [57]. According to Oroni [51], the hydrogen concentration in the traps C_T is given by

$$C_T = \theta_T N_T$$

where θ_T represents the degree of occupation of traps and N_T the trap density. From theoretical considerations, it is known that hydrogen atoms in the lattice and the traps are in chemical equilibrium, with the equilibrium is being mostly shifted to the side of the traps because of the high bonding energy between the hydrogen and the lattice defects.



Figure 5 Different hydrogen traps in the structure. a) Ideally solved in the grid. b) an alloying element. c) a transfer. d) a grain boundary. e) a phase boundary. f) a micropore with recombination to H_2

2.3.2. Diffusivity of hydrogen through the metal

In ideal solids, a general distinction can be made between three different diffusion mechanisms. The first mechanism is the vacancy diffusion, in which the atoms diffuse through the positions of the lattice vacancies. The second mechanism is the interstitial diffusion, in which interstitial atoms, such as hydrogen, occupy interstitial sites and change them rapidly. Since this mechanism is thermally activated, these changes occur more easily with increasing temperature. In the third mechanism, the exchange mechanism, two adjacent atoms in the crystal lattice directly exchange their places [49].

The value given in the literature for the diffusion coefficient of the lattice diffusion in pure α iron varies depending on the examination method and the degree of purity [50], [51]. Alloying elements such as Ni, Mn, Co and Cr decrease the diffusion coefficient of hydrogen in α -iron [52]. Kesten attributes the decrease of the hydrogen diffusion in α -iron to the interactions of the alloying elements with the hydrogen atoms [53]. Recent researches determine the diffusion constant of the pure lattice diffusion D_L in α -iron at room temperature to 7.5 * $10^{-5}c m^2/s$ [54].

In steels, hydrogen diffusion is primarily defined by the microstructural properties [55]. Steels with martensitic microstructure have a strongly inhomogeneous microstructure with a multitude of possible adhesion points for internal hydrogen. Therefore, in comparison to ferritic or bainitic structures they have a low hydrogen permeability. Measurements of the diffusion constant as a function of the microstructure show a reduction in the effective diffusion with rising carbon content [56]. At a relatively low carbon content of 0.23wt.%, the diffusion coefficient at 298 K is given as only $4.24 * 10^{-7} c m^2/s$.

Plastic deformation can also lead to a reduction in the effective diffusion rate through the formation of additional dislocations [57], [58]. The associated problem of the hydrogen transport in front of the crack tip has been numerically investigated by Sofronis and McMeeking [59]. They combined Oriani's equilibrium theory of hydrogen distribution with FEM-calculations of elastic-plastic deformation process before the crack tip. They have shown that large amounts of hydrogen are formed in the plastic zone in front of the crack tip during deformation. The decisive factor for the rise in the hydrogen concentration is the increase in the number of the hydrogen traps by more than 200 times. At the same time, the effective diffusion coefficient drops to 60 % of its initial value in pristine undeformed lattice diffusion.

It should be noted that the increase of the hydrogen concentration based on hydrostatic tensions is comparatively low. Therefore, it is not the hydrostatic tension, but primarily it is the plastic strain which influences the distribution as well as the concentration of hydrogen. If the relationship between the plastic deformation and the trap density is known, concentration profiles can be calculated ahead of the crack tip. Based on these results, one can conclude that the highest hydrogen concentration is generated directly at the front of the crack tip. The greater the increase in trap density, which is caused by the strain, the steeper is the concentration gradient of hydrogen.

Passive layers at the surface of metal are penetrable for atomic hydrogen, nevertheless they usually represent an obstacle to hydrogen permeation because of surface effects [60], [61]. Schomberg and Grabke examined the hydrogen permeation through a defined oxide layer of the type Fe_{1-x}O (0.06<x<0.11) at the metallic surface, whereby the oxide layers were each located at the outlet side of a 1 mm iron membrane [62]. They found out that the diffusion coefficient for hydrogen in these layers is $4 * 10^{-10} c m^2/s$. On the one hand, this means a considerable reduction of hydrogen uptake because of a shift in the equilibrium in Eq. (2.2h) in favour of recombination. On the other hand, it also means a reduction of the effective diffusion on the detection potential leads to the assumption that the hydrogen is present in the oxide layer as well as inside the metal as a proton [63].

2.4. Hydrogen embrittlement mechanism

The multitude lattice effects caused by hydrogen has led to the development of several models in which hydrogen traps, already discussed above, play a more or less central role. The following explanations give an overview of the most important models for iron and steel.



Figure 6 Pressure theory

This model, first presented by Zappfe and Sims, assumes that hydrogen recombination takes place inside the pores and microcracks thus causing very high local stresses [64]. Combined with the stresses resulting from external loading and lattice defects, the resulting pressure can overcome the bonding forces between neighboring atoms and thus promote crack formation. Moreover, this model also explains, for example, the formation of pickling bubbles on soft iron in ambient media with extremely high hydrogen activity.

2.4.2. Adsorptions theory



Figure 7 Adsoption theory

According to the Griffith Model for ideally brittle materials, the breaking stress is proportional to the square root of the surface energy. Consequently, and because of the purely thermodynamic reasons, hydrogen can accelerate material cracking by reducing its surface energy [64]. However, numerous arguments can be presented against the hydrogen adsorption theory. For example, some gases with a greater adsorption heat (e.g. oxygen) are less crack accelerating than hydrogen and thus can suppress the hydrogen effect partially or even completely [65].

2.4.3. HEDE (Hydrogen Enhanced Decohesion Embrittlement)



Figure 8 HEDE

In contrast to the adsorption theory, the HEDE theory includes the crack initiation nuclei in the areas of the metal close to the crack. This damage model considers cohesive forces between the iron atoms and the reduction of the bonding forces due to the interaction with the atomic hydrogen under the influence of high mechanical stress. This results in a purely elastic separation of the material. Such decohesive behavior can be explained by the changes in the electronic structure of metals. The atomic hydrogen gives up its electron and thus becomes a proton. The electrons are taken by transition metals with unoccupied inner shells. Consequential, in a state with increased internal energy this leads to a reduction of cohesive forces between the adjacent metal atoms. A low hydrogen concentration is sufficient for crack growth since the plastic deformability in the crack tip of high-strength steels is low and the tensile stress that occurs in the crack tip is high [22].



Figure 9 HELP

According to the HELP mechanism, material failure occurs through locally plasticized areas. These are caused by the inhomogeneous distribution of hydrogen in the material, since most hydrogen is found in the stress areas. This leads to a decrease in the elastic interactions between the hydrogen-affected dislocations and obstacles in the crystal lattice. The mobility of local dislocations is increased, which leads to the occurrence of high local plastic deformation, while macroscopically the deformation is small. This can cause local damage to the component. If the fracture surface is viewed with a high-resolution microscope after a brittle fracture has occurred, numerous local ductile deformations can be detected [30], [31].

In summary, the damage caused by hydrogen cannot be explained exclusively by any of the above discussed models. Rather, it is much more likely that several mechanisms develop simultaneously and interact with each-other, and, depending on the material and corrosion system, one mechanism predominates [20].

2.5. Formation of white etching cracks on the steel surface due to hydrogen embrittlement

The phenomenon known as white etching cracks (WEC) is one of the undesirable side effects during the operation of bearings. It leads to a drastic reduction in the bearing service life. All areas of the bearing application are affected, from industrial gearboxes, automotive gearboxes, POD drives for marine applications to air conditioning and dryers. Such failure is

also not attributable to a single type of steel, but occurs practically in all those used for the bearings [66]–[68]. The enormous damage caused by WECs can be illustrated using wind power plants as an example. 76% of wind turbine gearbox failures are due to the bearings, with WECs being the leading cause [67].

WECs are cracks with < 0.1-1 μ m width. A white etching area (WEA) with brittle flaking forms around the cracks, which shows a change in the microstructure. The WEA structure are nanosized ferrite grains with a diameter of 5-300nm, with a dispersion of carbide particles [7,6,24,67,68,98-100]. This area is supersaturated with carbon in the solid solution, which leads to a higher hardness of 10-50% than in the basic matrix [69]–[72]. The higher degree of hardness can be explained by the Hall-Petch relationship and by the dispersion of very fine cementite particles in the WTG [69], [70], [73].

Hydrogen embrittlement is the origin of WECs and promotes further crack propagation and flaking by supporting the plastic deformation of the steel [74]. As already described in detail, hydrogen diffusion and accumulation at grain boundaries and in the voids is the primary factor for hydrogen embrittlement of the host metal. From these results it can be concluded that in the absence of hydrogen no WEC is formed in the steel. Based on this finding, the question can be asked, what is the source of hydrogen in bearings and which factors prevent or promote hydrogen evolution? Numerous studies have been carried out on this question using different theories and approaches. Newlands [75] found out that hydrogen is a by-product of the decomposition of greases as a result of tribochemical reactions. Kohara [77] concluded that lubricity is critical because the lower the friction, the less nascent steel surface is created to catalyse the decomposition. These and other studies support the basic idea that hydrogen is the result of lubricant decomposition processes. Another hypothesis is that water as contamination in lubricants is the main reason for the WECs [78]–[80].

In the following sections, the two different models for hydrogen evolution are discussed.

2.5.1. The role of lubricants causing the white etching cracks

For the decomposition of lubricants and the reduction of water to hydrogen and other constituents nascent steel have the most decisive influence on the formation.. The friction between two steel surfaces, as is the case in ball bearings, continuously produces a fresh steel surface by removing organic contamination and oxide layers. Numerous active sites such as cations, anions, radicals and defects are present on this surface [81]–[84]. These active sites have a strong catalytic decomposition effect on organic substances [77], [85]–[87]. Morecroft [88] was able to demonstrate that organic molecules such as octa-, decane and butane decompose on fresh steel surfaces at room temperature, releasing hydrogen, methane and carbon monoxide.

Kohara [77] has shown with his series of experiments that the decomposition of the lubricant and the resulting hydrogen production do not depend on the chemical composition of the oil. The wearing of the metal is the decisive factor. The tests indicate that the hydrogen evolution is proportional to the wear surface. This finding leads to the conclusion that the amount of hydrogen produced depends on the lubricant's lubricity and not on its chemical structure. The better this property, the less fresh steel surface is produced, which is capable of catalyzing the decomposition of the lubricant and the reduction of water to hydrogen.

Lu's results [86] agree with those of Kohara. He also established a relationship between sliding speed, load and desorption of hydrogen. The desorption increases proportionally with the sliding velocity and parabolic with the load. In addition, with the sliding velocity, a proportional nascent surface is created at the same time.

In the same study, Lu [86] has established an approach for the mechanism of decomposition of oil chains, as shown in **Figure 10.** After the adsorption of the oil on the surface, the cleavage of C-C bonds follows, which results in the release of hydrogen and hydrocarbon gases.



Figure 10 Decomposition mechanism of hydrocarbon oil on the nascent steel surface [2]

2.5.2. The role of water causing the white etching cracks

Esfahani, et al. [89] and other research groups have investigated the influence of water on hydrogen production [78]–[80]. The obtained results indicate the essential contribution of water content in lubricants. Even the lowest water concentrations are sufficient to dramatically reduce the service life of steel. The results of Grunberg and Scott [90] show that 0.002 % of water content reduces the fatigue life of the steel surface to 48 %. The effects on bearings have also been investigated in many other studies [91]–[94]. An amount of 20 ppm water is found to be sufficient to reduce their fatigue life. The dissolved water reduces the functionality of anti-wear agents as well [95], which leads to increased wear and thus to the creation of a fresh steel surface. The water also promotes an acidic environment by converting sulfur phosphorus Extreme Pressure (EP) additives into acids [78], [96], [97]. This results in corrosion of steel and the generation of hydrogen as a by-product.

Haque [98] was able to prove in a series of tests, by mixing eleven additives in various combinations with a base oil, that water plays a decisive role in the formation of WECs. Depending on the combination of additives, in some samples WECs were formed after only 50 h. In other samples with a different selection of additives, the tests didn't detect a visible spread of WECs even after 500h of operation. After all samples were analyzed for their water content, it was observed that all samples that conveyed WECs in a shorter time window had an average water content 10-20 times higher than the others. Looking closely at the additives,

it was revealed that the samples with the longest test times contained no metallic additives (ZDDP (Zinc dialkyldithiophasphates), Ca/Na/Mg alkyl sulfonates). These additives have a hygroscopic effect, meaning that water from the air humidity or other sources can penetrate the oil. This finding confirms the important role played by water in terms of the occurrence of WECs.

With this in mind, Haque [98] has developed a mechanism for the dissociation of water (**Figure 11**). The lubricant transports the water directly to the steel surface where it dissociates due to the heat released by friction. The dissociated water is reduced to hydrogen at the nascent steel surface and additionally promotes the oxidative decomposition of lubricants [89], [99]. The hydrogen diffuses under the lubricated contact, where it enters the steel matrix. This lays the foundation for the initiation of hydrogen embrittlement and the formation of WECs and WEA.





Through conducting an extraordinary experiment Haque [98] was able to substantiate his hypothesis on the dissociation of water. For this purpose, he carried out experiments with oils

supersaturated with deuterium oxide (D_2O). The aim was to initiate WECs with D_2O and to detect the presumably formed deuterium in the cracks with a TDS (thermal desorption spectrometer). In fact, an amount of 0.06ppm deuterium could be detected. The reference oil, without the addition of D_2O , caused much smaller, practically 0ppm deuterium in the cracks.

Esfahani, et.al. [89] also demonstrates with his results the influence of water on the decomposition of lubricants **(Figure 12)** which confirms Haque's results. In this figure the line A represents the oil without water content, the line B has a water content of 5 % and the line C has been added 3.5 % NaCl in addition to the 5 % water. It is seen that these curves have different courses, and, at the same time, some similarities are also clearly visible. For example, irrespective of the composition of the oil, the development of hydrogen in all cases begins with the start of friction and stops when friction stops. It underlines once again the catalytic effect of the fresh steel surface created during the friction. As for the differences, it is quite noticeable how strongly the water promotes the development of hydrogen. While the oil A shows a moderate increase, the other two oils initially reach values that are 400-500% higher. Furthermore, it can be observed that the hydrogen permeation of oil A quickly adjusts to a constant level. While the other two oils do not reach constant values within five hours, they steadily decrease. One reason for this could be the uneven production of hydrogen on the surface, caused by the constantly changing ratio of the formation of corrosive products and the nascent steel surface caused by wear.





In summary, based on the conducted literature review, it can be said that both lubricants and water release hydrogen. However, it is important to mention that water, which is usually considered as a contamination in the lubricants, strongly accelerates the decomposition of the latter.

2.6. Permeation measurements



2.6.1. Operating principle of the Devanathan-Stachurski method

Figure 13 Set-up of the Devanathan & Stachurski techniq

In most cases, a diffusion measuring cell according to Devanathan and Stachurski [13] is used to perform permeation tests and determine diffusion coefficients. The schematic structure is shown in **Figure 13**. The material to be tested (thin plate) is positioned between two containers and separates them. The containers are each filled with an electrolyte solution and depending on the desired diffusion measurement, the necessary boundary conditions can be set. The hydrogen concentration must be kept at a constant value on the one side of the sample and at the same time it should be zero on the other side. In order to achieve this, the left-hand container is operated galvanostatically, which allows atomic hydrogen to be generated on the sample measuring surface. The diffusing hydrogen is oxidized on the outlet side of the platelet by an applied positive voltage. The detected oxidation current density is proportional to the amount of diffused hydrogen. In addition, information about the hydrogen concentration, the coverage of the surface of the inlet side and hydrogen traps in the material can be obtained from the permeation curve [13], [100], [101].

2.6.2. Palladium deposition

The need for a palladium layer on the exit surface of metal membranes is often discussed in the literature [61], [102]–[104]. If a palladium coating is not applied, a passive layer can be formed on the surface, which will act as a barrier to the hydrogen diffusion. In order to minimize the possibility of a passive layer formation, a palladium coating is preferred. Another disadvantage of not using palladium coating in the membrane surface is the possibility of incomplete oxidation of the hydrogen. A basic idea behind the permeation measurement assumes that the hydrogen diffusing through the membrane is immediately oxidized on its outlet side according to equation (2.6a) [102].

$$H \to H^+ + e^- \tag{2.6b}$$

Incomplete oxidation can, however, impair the traceability of the measurement, since in such cases, according to equation (10), a recombination of H to molecular hydrogen can occur [102].

$$H + H \to H_2 \tag{2.6b}$$

In this case, the resulting molecular hydrogen is not detected and thus the amount of diffusing hydrogen is not fully recorded. Such recombination can be also observed visually by viewing bubble formation at the surface on the exit side of the membrane [102].

In the literature different experimental parameters such as the change of the electrolyte, or a variation of the applied loading current density have been investigated [102],[105]. Practically in all these experiments a strongly increased hydrogen flow through metal membranes coated with a palladium layer was always measured.

There are several ways to apply the palladium coating, such as electrochemical deposition and sputtering using the PVD process.

2.6.3. Evaluation of the data

In the classical permeation technique developed by Devanathan-Stachurski in Ref. [13], a thin metal membrane of thickness L [cm] is positioned between two independent electrochemical cells. Hydrogen is introduced In the loading cell (the input side at x = 0) and then diffuses towards electrolyte-metal interface. After getting through the membrane hydrogen is immediately oxidized in the oxidation cell (the output side at x = L). It should be noted that a passive layer can be created on the outlet side or a palladium top layer can be applied for capturing released electrons in the oxidation reaction. Homogeneous platelets are mostly used as possible cover layers. In addition, evaluation methods are solved under the following boundary conditions: a constant hydrogen concentration c_1 = const on the loading surface, and a zero concentration $c_1 = 0$ on the exit side of the platelet. In this thesis we focus on the effect of several important parameters on the obtained results. The first important parameter is the effective diffusion constant D [cm²/s], which can be calculated using the Time lag T_{lag} [s] method [25]. Time lag is the time necessary for the hydrogen permeation rate to reach 0.63 % of the steady state. This relationship is described by the Einstein diffusion relation (2.6a).

$$D = \frac{L^2}{6T_{lag}}$$
(2.6a)

Once D has been calculated, the second important parameter, the breakthrough time t_b [s] can be determined. This is the time necessary for hydrogen to reach the output side (2.6b).

$$t_b = 0.924 \frac{L^2}{\pi^2 D}$$
(2.6b)

In case of thermodynamic equilibrium between the loading surface of the membrane and electrolyte, the concentration of diffusible hydrogen in the membrane at its entry c_0 [mol/cm³] can be calculated via the diffusion coefficient and the achieved stationary current density. This is done using the equation (2.6c):

$$c_0 = \frac{j_{\infty}L}{FD}$$
(2.6c)

Where c_0 is the surface concentration of hydrogen [mol/cm³], j_{∞} is the stationary current density [A/ cm²] and F is the Faraday constant [96.485 C/mol][106].

The fourth important parameter is the total hydrogen mole per square centimeter diffusing through the membrane, which can be easily calculated by integrating the current density (2.6d) [107].

$$S = \frac{1}{Ft} \int_0^t j dt \tag{2.6d}$$

Here **S** is total hydrogen mole per square centimeter [mol/cm²], **j** is the current density $[\mu A/cm^2]$ and **t** is the time [s].

3. Experimental procedure

3.1. Sample materials

The following materials were used: steel foil (25μ m thickness), palladium foil (25μ m thickness), 0.1M NaOH, ammonium chloride NH₄Cl, ammoniac NH₃, palladium chloride PdCl₂, acetone, 37% HCl 1:1 with water, 3,5% NaCl solution with pH6, filter paper (blue line) separator (125μ m), BO318 oil + A +B + C and perfluorinated polyether oil (PFPE), where the notation A, B and C stand for:

- A = Anti-oxidation additive
- B = Anti-wear additive
- C = Anti-corrosion additive

3.2. Preparation of the samples

3.2.1. Preparation of the working electrode

During the experimental work of this master thesis **two** different types of working electrodes were used, a steel and palladium foil. All the samples have been cleaned with the same chemicals and in the same order. At first, it was washed with acetone, followed by a 0.1M NaOH solution, then again with acetone and at the end with an HCl solution (1:1). Between these cleaning steps, the samples have been washed with distilled water except after acetone. The steel foil had the following composition (**Table 1**).

| Elements | С | Mn | Р | S |
|-------------|------|-----|-------|-------|
| Weight in % | 0.12 | 0.6 | 0.045 | 0.045 |

Table 1 Composition of the steel foil

3.2.2. Preparation of the palladium electrolyte solution

The following recipe for the Pd bath was chosen:

PdCl₂: 25g/L NH₄Cl: 20g/L NH₃ (25%): 250ml/L

The solution was prepared as follows:

The first step was to dissolve the $PdCl_2$ powder at heating and stirring in the NH_3 solution until the solution turned transparent and yellow. Next, the NH_4Cl was added to the solution. The final volume of the electrolyte was reached by adding distilled water. If the pH value is below 9, NH_3 was added until the needed value is reached.

3.2.3. Deposition of palladium layer on the steel membrane

To ensure complete oxidation of the diffusing hydrogen and to prevent the recombination of atomic hydrogen to molecular hydrogen, the sample exit side was coated with palladium. Two different approaches were tested.

3.2.3.1. Galvanostatic approach

The sample was fixed between two supporting rings. A specially designed holder attached the ring to a glass cell, which was equipped with a platinum counter electrode **Figure 14**. Before coating, the sample first had to be cleaned (see section 3.2.1.). The sample was electrically switched on as a cathode while the platinum plate served as the anode. The current density of the reduction process was 5 mA/cm² and the metal platelet was coated with Pd for 8 minutes, resulting in a layer thickness of 1 μ m.



Figure 14 Design of the cell for the galvanostatic deposition

3.2.3.2. Physical Vapor Deposition PVD

Alternatively, a coating by means of PVD processes was also carried out. For this purpose, a palladium target was installed in the coating system (BAL-TEC MED 020) and the sample holder (2 samples per coating cycle) was placed. The sputtering process was performed at room temperature and under a pressure of $2 \cdot 10^{-2}$ mbar in the chamber. During the sputtering a current of 100mA was applied and the coating chamber was filled with argon gas. The Ar⁺ ions produced by impact ionization were accelerated by the voltage of the applied current in the direction of the palladium target and knocked the atoms out of the target by an impulse transfer, which eventually could deposit on the substrate. After the test duration of 3 minutes, the steel sample was covered with a palladium layer of about 1 nm thickness.

3.3. Practical use of the Devanathan-Stachurski cell

3.3.1. Using an aqueous solution in the input cell

A schematic diagram of the diffusion measuring device is shown in **Figure 15.** The coated sample was positioned between two glass cells and fixed with two plexiglass rings and a

clamping device. A 0.1M NaOH solution was used as the medium in the oxidation side and a 3.5% NaCl solution with pH6 in the loading side. During some experiments, the solutions were additionally purged with nitrogen. Platinum was used as the counter electrode in both cells and a Hg/HgO was used as the reference electrode in the output cell.

A potentiostat "Autolab PGSTAT302N " from Metrohm Inula was used to record the oxidation current and set a constant load current. Before the actual diffusion measurement began, the residual current was measured. For this purpose, the 0.1M NaOH solution was filled into the oxidation cell and an oxidation potential of + 0.28V relative to the Hg/HgO electrode was set using the potentiostat. After 700s the loading cell was filled with the KCI solution. Once 2000s passed, the loading current density either 5mA/cm² or 10mA/cm² was applied and the permeation measurement was initiated, using a "Keithley 2450 SourceMeter". An increase in the oxidation current was observed after the start, which reached a constant value after some relaxation time. The charging current was interrupted after 75 min, followed by a strong decrease of the oxidation current. As soon as the resulting decay curve reached a constant value, the experiment was stopped and the sample was removed from the chamber.



Figure 15 Construction of the permeation cell for the permeation measurements with aqueous solution: (a) steel foil, (b) platinum counter electrode, (c) Hg/HgO reference electrode, (d) output cell, (e) input cell
3.3.2. Using a non-aqueous solution in the input cell

The experimental setup for the measurements with non-aqueous solutions has been designed to ensure close contact between the working electrode and the counter electrode. While the preparation of the sample did not change, the setup differed slightly. While the output cell stayed the same, the input cell was adjusted to the non-aqueous solution (**Figure 16**). As illustrated in the picture, the input cell consisted of a filter paper, the working and counter electrode between the two Teflon rings. The filter paper acted as the storage for the non-aqueous solution. 30 drops of the tested solution were dropped on the filter paper. The steel foil (working electrode) had a thickness of 25µA and was pretreated, as previously described. The sample was placed with the non-layered site on top of the filter paper. Finally, the Teflon rings were fitted between the output cell and the holder. Once the cell was ready, the counter electrode of the input cell was brought into contact with the soldering iron "ProsKit SI-131B" (**Figure 17**).



Figure 16 Construction of the permeation cell for the permeation measurements with non-aqueous solution: (a & e) platinum counter electrode, (b) filter paper, (c) steel foil, (d) Hg/HgO reference electrode, (f) output cell, (g) input cell and (h) seal ring



Figure 17 Final experimental setup with the soldering iron on the left side and the cell on the right side of the picture.

As in the measurements with the aqueous solution, the output cell is filled with a 0.1M NaOH solution and polarized with + 0.28V. However, different test series were carried out with non-aqueous solutions, on the one hand with the BO318 oil and on the other hand with the PFPE In the following sections, the respective test procedures are described in detail.

3.3.2.1. Using the BO 318 lubricant

Before the actual diffusion measurement using the steel foil began, the residual current was measured for 40min. Immediately afterward the soldering iron was turned on to raise the temperature of the steel foil to 100°C. Right away, the oxidation current increased. One hour was waited for the measured current to reach lower values before applying 40V to the input cell to initiate the permeation measurement. A slow increase in the oxidation current was observed after the start. The charging current was interrupted after 70min and a strong decrease of the oxidation current could be observed. As soon as the resulting decay curve reached a constant value, the experiment was stopped and the sample was removed from the chamber.

3.3.2.2. PFPE

For the experiments with PFPE, a palladium foil was also used as the working electrode in addition to the steel foil. The performance of the measurements did not differ from that of BO 318. Only the times for performing individual steps were adjusted. Different approaches were used here.

Steel foil as the working electrode:

- The residual current was measured overnight between 15 and 17 hours. Once the temperature was on, the polarization with 30V was started after three hours instead of one. The loading current was also interrupted later after three hours.
- 2. The filter paper was dried in an oven for 30min and 16 hours at 150°C. The residual current was measured for an hour. Once the temperature was applied, the voltage of 30V was switched on as well after an hour. The sample was polarized for four hours until the voltage was turned off.
- 3. The same procedure was performed as described in the second point. The only difference was that the coating of the steel foil with palladium was not done galvanically but by the PVD method.

Palladium foil as the working electrode:

- The same procedure was carried out as with the second series of tests with the steel foil. Only that the filter paper was dried for 30 minutes together with the palladium foil.
- In this test of series, the output cell was purged with nitrogen, otherwise the procedure stayed the same. During the measurement, the nitrogen flow was repeatedly turned on and off after 7500 s to investigate the effect on the detected current.

3.4. Evaluation of the obtained results

In **section 2.6.3.** of the theoretical part, the important parameters with which the obtained curves are evaluated were described. **The Graphic 1** below presents the necessary data for the evaluation.



Graphic 1 Determination of parameters from a hydrogen permeation curve for the calculation of further parameters

If one observes the permeation current curve, it is essential to subtract the residual current j_0 from the maximum value reached by the current. In overall, an absolute current increase is obtained. By subdividing the steady-state value j_{∞} in 63 percent, the respective time lag can be determined, for example, to calculate the effective diffusion coefficient (equation (2.6a)). By inserting the variables in equation (2.6b), (2.6c), or equation (2.6d), the remaining parameters can be calculated. The calculation procedure is summarized again as follows:

Calculation of the effective diffusion constant D [cm²/s]

$$D = \frac{L^2}{6T_{lag}}$$

Sample thickness L

= 0.0025cm

• Calculation of the breakthrough time *t_b*

$$t_b = \frac{L^2}{15.3D}$$

Calculation of the concentration of diffusible hydrogen in the membrane at its entry *c*₀ [mol/cm³],

$$c_0 = \frac{j_\infty L}{FD}$$

| the stationary respective current density j_{∞} | = $2.5 \cdot 10^{-5}$ A/cm ² |
|--|---|
| Faraday constant F | = 96485C/mol |

• Calculation of the total hydrogen mole per square centimeter **S** [mol/cm²]

$$S = \frac{1}{Ft} \int_0^t j dt$$

| Experiment | t _{lag} [s] | t _b [s] | c ₀ [mol/cm ³] | D[cm²/s] | J∞[μA/cm²] | S [mol/cm ²] |
|-------------|----------------------|--------------------|---------------------------------------|----------|------------|--------------------------|
| 1. 10 mA N2 | 107 | 60.1 | 9.0 E-5 | 9.7 E-9 | 33.8 | 1.49 E-6 |

4. Results and discussions

4.1. Using aqueous solution in the input cell

This section concentrates on the performed experiments using a 3.5% NaCl solution in the input cell.

4.1.1. 3,5 % NaCl solution with pH 6

The **Graphic 2** compares all results of the measurements, obtained using the 3.5% NaCl solution in the input cell. The gained results demonstrate that by varying the boundary conditions different values were achieved. Only after doubling the cathodic current on the input cell from 5 to 10 mA, no difference is noticed.

The most apparent effect on the permeation of hydrogen in these measurement is the variation of the membrane thickness by 20 times from 25 to 500µm (**Graphic 4**). The maximum achieved value is about 5-7 times smaller compared to the other maxima. It must be taken into account, that the stationary state was not reached in these two measurements. It was deliberately measured in a certain time window for a better comparison of all measurements. Furthermore, one notices the slow rise of the measured oxidation current after switching on the cathodic current and the slow decrease once the current is switched off again. This is due to the increased path length that the hydrogen has to pass through. It can be explained by the theory of "random walk", which states that the probability of a particle moving in one direction is the same for all directions. With this in mind, by increasing the thickness of the steel foil the probability to arrive at the other side of the foil is reduced, since the space was increased to move randomly in the lattice structure.

The following experiments were performed by applying a current of 5 and 10mA using again a 25µm thick steel foil. According to the measured values shown in the **Graphic 3**, doubling the cathodic current does not affect the HER data. This conclusion actually contradicts the theory. The latter assumes that the doubling of the current doubles the number of electrons at the cathode. For this reason, the degree of coverage of the cathode surface with chemisorbed hydrogen should also increase. As mentioned in section 2.2.3. the chemisorbed hydrogen is absorbed according to the "Hydrogen Absorption Reaction". As a result, the concentration of hydrogen in the metal should increase, and eventually the oxidative current as well. This contradiction is probably attributable to the sealing ring that prevents the solution from leaking out of the membrane (**Figure 16 (h)**). While filling the cell with a solution, small air bubbles are formed at the contact between the steel foil and the ring. To a certain extent, the bubbles can be removed by shaking the sample. However, in most experiments, a small amount of air bubbles remained intact. The quantity and size of them were always different and could not be influenced in a controlled manner. The problem arising with the bubbles was the inhomogeneous coating of the WE with palladium by electroplating. Once the output cell was filled with NaOH solution after the palladium coating, two different outcomes were possible. The first one, bubbles were formed again at the same spots. As a result, a lower current is measured, because of a smaller surface area of the coated palladium. Second one, no bubbles are formed. The uncoated steel surface comes in contact with the NaOH solution. A higher current is measured due to local corrosion.

The **Graphic 4** demonstrates the gained results when the output cell was additionally purged with N_2 gas. In contrast to the results from **Graphic 3**, the obtained maxima of the curves are slightly less in magnitude. To understand this result properly, it is important to know which reaction took place at the counter electrode in the output cell. It is assumed that in the reaction

$$2e^{-} + 2H_2O \rightarrow 2OH^{-} + H_2$$

hydrogen is generated at the counter electrode. Part of this hydrogen diffuses through the solution to the working electrode, where it is oxidized together with the atomic hydrogen, which is permeating through the WE from the input cell. By purging the output cell with N₂ gas, some of the generated hydrogen at the counter electrode escapes from the solution without coming in contact with the working electrode. This leads to a smaller amount of the detected current.

In summary, the results obtained by purging the output cell with nitrogen ensure a more reliably date. The thicker the sample, the lower and slower is the diffusion of the atomic hydrogen through the membrane. Finally, the comparison between 5 and 10 mA cathodic current is not meaningful in these series of tests. This summary is underlined by the calculated parameters in the **Table 2**. Whereby the parameters for the 500 μ m steel foil were not calculated, since a stationary state was not obtained.



Graphic 2 Comparison of all results with 3,5 % NaCl solution in the input cell



Graphic 3 Results of two experiments for each applied current of 5mA and 10mA with 3,5 % NaCl solution in the input cell using 25µm steel membrane.



Graphic 4 Results of three measurements with 10mA and 3,5 % NaCl solution in the input cell and purging the output cell with N_2 using 25µm steel membrane



Graphic 5 Results of two experiments for 100mA with 3,5 % NaCl solution in the input cell and using $500 \mu m$ steel membrane

| Exp | eriment | t _{lag} [s] | t _b [s] | c₀ [mol/cm³] | D[cm²/s] | J∞ [μA/cm²] | S [mol/cm ²] |
|-----|----------|----------------------|--------------------|--------------|----------|-------------|--------------------------|
| 1. | 10 mA | 276 | 155 | 2.8 E-4 | 3.8 E-9 | 40.6 | 1.71 E-6 |
| 2. | 10 mA | 218 | 122 | 2.1 E-4 | 4.8 E-9 | 38.1 | 1.60 E-6 |
| 3. | 10 mA N2 | 33 | 18.5 | 2.6 E-5 | 3.2 E-8 | 31.4 | 1.48 E-6 |
| 4. | 10 mA N2 | 107 | 60.1 | 9.0 E-5 | 9.7 E-9 | 33.8 | 1.49 E-6 |
| 5. | 10 mA N2 | 32 | 18.0 | 2.7 E-5 | 3.3 E-8 | 34.3 | 1.53 E-6 |
| 6. | 5 mA | 306 | 172 | 3.4 E-4 | 3.4 E-9 | 44.27 | 1.84 E-6 |
| 7. | 5 mA | 387 | 217 | 3.8 E-4 | 2.7 E-9 | 39.63 | 1.59 E-6 |

Table 2 Calculated parameters using a 3,5 % NaCl solution in the input cell

4.2. Using Non-Aqueous fluids in the input cell

This section concentrates on the performed experiments using the oils BO318 and PFPE in the input cell.

4.2.1. BO 318 + A + B + C additives lubricant

The **Graphic 6** illustrates the results of the experiments carried with the BO 318 oil. For a correct interpretation of the results it is important to have a look at the composition of the oil. The oil contains three additives A, B and C. Two of these additives have hygroscopic properties contaminating the oil with water. During the cathodic polarization of the steel sample, the water is reduced to hydrogen at the WE, which explains the increase of the oxidation current after 6000s. The detected peak at 2700s can be explained with the rising temperature. As a result of the applied thermal energy, trapped hydrogen is released from reversible traps in the steel structure and thus was measured by the potentiostat at the anodic side of the WE (see section 2.3.1.).

The gained results show a division of the curves into two sections. The blue to red-colored curves display a higher permeation flow than the green colored ones. The large dispersion of the curves is due to the following factors.

1. Inhomogeneous palladium coating:

The inhomogeneous palladium coating has a significant effect on the measured oxidation current. As described in the previous section, it can lead to the formation of corrosion on the exit side. The resulting electrons are detected by the potentiostat and distort the result, depending on how much corrosion has formed.

An alternative way to avoid this source of error is to coat the steel membrane with the PVD process. This enables a homogeneous coating of the complete membrane. This is discussed in more detail in the section 4.2.5.

2. Unknown oil volume:

Before each test, the same amount of the base oil BO 318 was spread over the filter paper. However, by pressing the Teflon rings together and heating the set-up to 100°C,

during the experiment, the oil was leaking extensively between the rings. As a result, the remaining oil volume may vary from experiment to experiment and, consequently, the amount of water that is reduced to hydrogen as well. With the present set-up, this problem cannot be solved.

3. Residual current:

The curves illustrate the influencing role of the residual current. A clear trend can be seen here. The lower it is before the temperature is increased and the voltage is applied, the more reliable the measurement results are. While the reddish and bluish curves have a higher residual current, they also show a much more drastic increase in oxidation current as soon as heating is applied. The increase is twice as large, sometimes more than ten times as large, as that of the greenish curves. The further course of the curves is also determined by the residual current. At the time, when the voltage of 40V is applied, the residual current of the red and blue curves is still higher without having reached a constant value. As a result, the curves briefly reach a maximum and then continue to fall. Whereas the green curves reach a stationary state after a short time. This is because their residual current has reached a stable value before the voltage was applied. For this reason, the parameters **D**, t_b , t_{lag} , j_{∞} , and c_0 could only be calculated for the lower curves (Table 2). Nonetheless, it must be mentioned that the currents are too small to calculate reliable values. Nevertheless, the parameters have been calculated to give a comparison to the previous results. The serious deviation of the residual curves is most probably due to the inhomogeneous palladium coating and the corrosion associated with it. To counterbalance this, the residual current can be measured for a longer period of time to give the system enough time to reach a steady-state.

In summary, it can be said that due to the numerous sources of error, the results are not reproducible and therefore not representative. Nevertheless, when the calculated parameters are compared with those of the previous test series obtained under the same conditions (25µm steel foil, without purging with N₂), the values for **D**, t_b , and t_{lag} are approximately of the same order of magnitude. Based on these findings, the rough claim can be made, that the diffusion constant for the diffusion of hydrogen through the used steel with a thickness of

 $25\mu m$ is in the order of $10^{-9} \text{ cm}^2/\text{s}$. A more accurate statement can be made if reproducible measurements are available.



Graphic 2 Results with the BO 318 oil using $25\mu m$ steel foil

| Experiment | t _{lag} [s] | t _b [s] | c₀ [mol/cm³] | D[cm²/s] | J∞ [μA/cm²] | S [mol/cm²] |
|------------|----------------------|--------------------|--------------|----------|----------------|-------------|
| 1. BO318 | 323 | 181 | 3.2 E-5 | 3.2 E-9 | 3.99 | 1,56 E-7 |
| 5. BO318 | 452 | 254 | 3.3 E-5 | 2.3 E-9 | 2.95 | 1,10 E-7 |
| 6. BO318 | 639 | 359 | 2.4 E-5 | 1.6 E-9 | 1.54 | 6,14 E-8 |
| 9. BO318 | 531 | 298 | 1.2 E-5 | 2 E-9 | 0.88 | 3,09 E-8 |

Table 3 Calculated parameters using BO318 oil in the input cell

4.2.2. PFPE lubricant

In this and the following sections, PFPE oil was selected as the base oil for the following tests. Compared to the BO318 oil, it has no additives which makes it water repellent. Furthermore, the molecular structure does not contain any H atoms. With these facts, it can be assumed that no rise of the oxidative current will be detected after the cathodic polarization of the WE in the input cell. Therefore, the oil is used as a reference to examine the accuracy of the D&S measuring technique. In this test series, the current was measured overnight for about 16 h to achieve the lowest possible stationary residual current.

A look at the curves in the **Graphic 8** reveals that half of the curves show the opposite of the expectation. An increase in the oxidation current after applying 30V is observed. By observing the WEs corresponding to these curves, they appear to be corroded at the cathodic side (**Figure 18**).

The obtained data supports the fact that the rising oxidation current is due to corrosion. A comparison between the measurement results gained by the BO318 oil and the PFPE oil is sufficient. The difference between these two oils becomes apparent in the section where the voltage is applied to the input cell. In the case of the test series with the BO318 oil (Graphic 6), the oxidation current increases immediately after the application of the voltage and decreases drastically after the voltage is switched off. This indicates that the HER on the input side is dependent on the external voltage. In the case of the test series with the PFPE oil (Graphic 8), the increase in oxidation current is independent of the voltage. The detected current increases from experiment to experiment at a different time after applying the voltage. The oxidation current of the green curve has a sudden rise even before any voltage was applied. In particular, there is no stop of the rise after switching off the voltage. The current increases until the setup is removed from the soldering iron. As a result, the temperature is the main factor. The Figure 18 proves the connection with the temperature, as the corroded surface reflects the contact surface to the soldering iron. Experiments under the same conditions performed by Prof. Dr. M. Monev and Dr. L. Mirkova, IPC, BAS, Sofia, Bulgaria, partners in the project, show similar outcomes (Appendix 1).

At this point, it is appropriate to ask the following two questions.

- Is the corrosion due to the influence of water or does the PFPE oil play a more important role?
- If it is caused by water, where does the water contamination come from, if the oil is supposed to be free of it?

1. Corrosion by the PFPE oil:

According to the literature, there is a possibility of a corrosion process by decomposition of the PFPE oil with the formation of FeF₃ on the steel surface, which catalyzes further decomposition of the PFPE oil. However, certain conditions are necessary for this to happen, which are not met in these series of tests. The decomposition of the oil is catalyzed either by α Fe₂O₃ or by freshly formed steel surface [114]-[116]. Moreover, high temperatures well above 100°C are required at the interface between the metal surface and the PFPE oil [116], [117]. The molecular structure of the polymer chain has the most influence on the decomposition. If a linear polymer chain is present, it can be attacked catalytically by FeF₃ as a Lewis acid. In contrast, branched chains are protected against such attacks [118]. Since the temperature during the experiments did not exceed the 100°C limit and a branched oil was used, decomposition of the oil can be excluded.

2. Corrosion by water:

The water in our set-up can come from two different sources. A part of the water quantity is due to the humidity of the air. The other part, which is more predominant, comes from the filter paper. An analysis according to Karl-Fischer Din 51777 by "Klüber Lubrication München SE & Co. KG" has shown, that the amount of water in the filter paper is high enough to cause corrosion of the steel.

To eliminate the water content from the filter paper, in the next series of tests the filter paper was dried in an oven at 150°C before use.

3. Temperature variations:

To ensure that the soldering iron kept the temperature constant during the test, the temperature between the WE and the filter paper in the input cell was recorded with a thermocouple. The Graphic (**Appendix 2**) shows that a constant temperature is guaranteed over five hours.

4. Pretreatment of the metal sample:

The samples were immersed for three minutes in a 0.1mol NaOH solution and 15s in a HCl solution. Meanwhile, the treatment with HCl is very aggressive, under which a high hydrogen evolution on the surface of the steel takes place. The resulting hydrogen is absorbed by the steel and is responsible for a higher residual current as well. With the reduction of the pretreatment time in the solutions to 1 second, the hydrogen development and thus its absorption by the metal can be reduced.

In conclusion, the rise of the oxidation current refers to corrosion processes. Whereby the filter paper acts as a source for the required amount of water. The reaction can be counteracted by drying the filter paper. Additionally, the residual current can be further reduced by shorter pretreatment times of the samples.



Graphic 3 Results with the PFPE oil without drying the filter paper



Graphic 4 Results with the PFPE oil without drying the filter paper after the rise of temperature



Figure 18 Corroded steel WE and filter paper after an experiment

4.2.3. PFPE lubricant impregnated on dried filter paper

As summarized in the last section 4.2.2, for this series of experiments the pretreatment time of the samples in the NaOH and HCl solution was reduced to one second each. Additionally, the filter papers were dried in an oven at 150 °C. One part was dried for 30 min and the other overnight for about 16 h. The results were then summarized and compared in the **Graphic 9**.

Due to the shorter pretreatment time, it was possible to reach a residual current lower than $1 \mu A$ in less than one hour. In the previous test series, in most cases, it took several hours to reach this value. With this approach, the measurement time was considerably reduced.

Regarding the drying of the filter paper, no corrosion was reported anymore, and with this no rise of the oxidation current after applying heat and voltage. Comparing the gained curves, no difference is noticeable between the measurements where the filter paper was dried for 30 min or 16 h. The **Graphic 10** underlines this by showing the values measured after five hours. In both cases, the detected current is in the range between 0.3 and 0.6μ A/cm². Because of the small scattering, one can say that the experiment is reproducible. The scattering of the values is based probably on the inhomogeneous coating of the surface with palladium, which partly causes corrosion in the uncoated areas on the exit side.

In conclusion, it can be said that effective measures have been taken by reducing the residual current and preventing corrosion on the cathode side of the sample. The reproducibility obtained proves the sensitivity and the functioning of the D&S method used.



Graphic 5 Results with the PFPE oil with dried filter paper



Graphic 6 Comparison of data after five hours measuring between experiments with dried filter paper for 30 min and 16 h

4.2.4. PFPE lubricant: dried filter paper and Pd coated steel foil by PVD

For this series of measurements, the samples were coated with the PVD method. There is a clear difference to the conventional method, both optically and in terms of measurement. The palladium coating has a darker homogeneous gloss, and the color is also more similar to that of steel than to palladium. Besides, the adhesion between the steel and the coating is very weak, so that the coating can be removed with a tissue without much effort (**Appendix 3**). Considering these observations, it can be assumed that the coating has failed and that no pure palladium coating has been obtained. The measurement data (**Graphic 11**) confirms that the palladium layer is not homogeneous. This becomes clearer when the results are compared with those from the section 4.2.3 in the separate **Graphic 12**. The measured values are more than twice as high. Assuming an inhomogeneous palladium layer, corrosion processes on the surface are a possible reason for the increased measured current. Due to the contact of the partly uncoated steel surface with the 0.1M sodium hydroxide solution, the formation of a passive layer under the following reaction

 $Fe + 2OH^- \rightarrow Fe(OH)_2$

Anode: $Fe \rightarrow Fe^{2+} + 2e^{-}$

Cathode: $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$

$$\sum : Fe + \frac{1}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2OH^{-}$$

is unavoidable. As the reaction equation shows, Fe is oxidized to Fe²⁺ at the anode, and the released electrons are detected by the potentiostat.

The reason for an incomplete palladium layer is the sputtering time. As mentioned in section (3.2.3.2), after three minutes of sputtering a layer thickness of only 1 nm is achieved. According to the literature [106], however, a thin sputtered layer thickness shows a non-covering layer with pores and holes. To avoid this problem, the application of a thicker layer is recommended.

In conclusion, it can be said that this series of tests are not representative, as no homogeneous continuous palladium layer was obtained.







Graphic 8 Comparison of the results by coating the steel foil with PVD and electroplating

4.2.5. PFPE lubricant: dried filter paper and Pd foil as the WE

The following experiments with the palladium foil act as a reference for the steel film with the electrocoated Pd layer. These are represented in the **Graphic** 13. The following characteristics of the curves can be observed:

1. A good reproducibility is achieved

- 2. An increase in current is detected after the start of the heating period.
- 3. A constant current is measured within less than half an hour after the rise of temperature.
- 4. No change is noted after applying the voltage of 30V.

At the first sight, everything seems to be conclusive. There is a reproducibility after eight measurements. A very low current of about 0.6 µA is measured and applying a voltage does not cause an increase. However, the question arises why primarily a current is measured and why an increase in current occurs during heating, as there are many reasons against it. First of all, one would think that it is the trapped hydrogen in the metal that is released by the increased activation energy. This assertion can be refuted with two arguments. Firstly, only one specific palladium foil was used for all the measurements. By using the same foil over again, the detected current would have to decrease from experiment to experiment, since there was no pre- or post-treatment of the foil, which supplied the material with new hydrogen. On the other hand, even the first measurement should have shown a faster decrease in current throughout the measurement. Corrosion processes on the surface can also be excluded, as palladium is a noble metal. Furthermore, the measured current cannot have its origin in the input cell. For this, water has to be present, either to be reduced due to the applied voltage or to initiate corrosion. As mentioned, corrosion can be excluded and the application of the voltage does not cause any change. All these reasons indicate that, contrary to our results, no current should be measured.

Comparing the measurement data obtained with those from sections 4.2.1 and 4.2.3, commonalities become apparent. The **Graphic** 14 represents this comparison. After two hours of measurement, the curves of the three-test series slowly coincide. After five hours, as the **Graphic** 15 shows, the measured values are in the same range and show almost the same mean and median values (Appendix 4 and 5). It can be assumed that the measured current for

all experiments after five hours does not correspond to the origin of hydrogen released from defects in the steel structure. The possible cause could be the applied voltage between the working electrode and the counter electrode in the output cell. Thanks to the voltage at the output cell, water is reduced to hydrogen at the counter electrode. By diffusing through the solution to the anode it gets oxidized. A self stimulating system is formed. The electrons go from the anode to the cathode, where there are utilized for repeated reduction of water. The increase in temperature of the setup increases not only the reaction speed but also the formation of convectional flow. This convection enhance the hydrogen transport from the cathode to the anode. This conclusion explains not only the measured oxidation current, but also its increase with temperature.

The assertion made above can be supported by the prevention of the hydrogen diffusion from the cathode to the anode. Using the palladium foil as the WE no current should be measured using the PFPE lubricant. This can be achieved by purging the output cell with nitrogen. The previous results in section 4.1.1 already show that when nitrogen is introduced, a more accurate current is measured.



Graphic 9 Results with the PFPE oil using a palladium foil as the WE



Graphic 10 Results with the PFPE oil comparing of the results of different test series



Graph 11 Comparison of data after five hours measuring between experiments of different test series

4.2.6. PFPE oil: output cell purged with N₂, dried filter paper and Pd foil as the WE

As described in the previous section (4.2.5.) the approach in this section is to purge the output cell with nitrogen, to observe a change in the current. The **Graphic 16** shows the result of the measurement.

Although the output cell has been continuously flushed with N₂ since the beginning of the measurement, the curve hardly differs from the data of previous measurement data without the N_2 purge (section 4.2.5). By increasing the pressure after 7500s from 0.4 to 0.6bar, a drastic decrease of the oxidation current can be seen. This is the first indication that the diffusion process of the generated hydrogen from the cathode to the anode was disturbed by the increased inflow of N_2 . This results in a lower detected current. After another 1020s (17 min) the N₂ flushing was completely closed. As a result, the curve rises steeply during the next 1380s (23min) until the N_2 was reintroduced. The oxidation current has reached a new maximum in this short time and would have increased even more if the cell would not be purged again with N_2 . This observation supports the finding that the hydrogen generated at the counter electrode diffuses to the anode where it is measured. Furthermore, with the help of the new maximum reached, it can be argued that the detected current from the beginning of the measurement would be higher in the absence of N_2 . In the further course of the experiment, the N₂ purge was turned off and on every 900 s (15 min). The previous observation was always repeated. In the absence of N_2 the current increased. As soon as the output cell was purged again with N2, the detected current decreased. After 14400 s the curve has not risen immediately after an additional N_2 purge, as usual, but has fluctuated until a slow increase was noted. This was due to the fact, that the 0.1M NaOH solution in the output cell had evaporated so much that, the working and counter electrodes were only half covered with the solution. As a result, the experiment had to be stopped and the measured data at the end of the experiment are no longer representative.

In conclusion, this experiment confirms the hypothesis that the hydrogen generated at the counter electrode of the output cell potentially falsifies the measurements because of being measured at the anode.



Graphic 12 Results with the PFPE oil using a palladium foil as the WE by purging the output cell with nitrogen



Graphic 13 Comparison of all measurements gained by using the palladium foil as the WE

5. Conclusion

The main focus of this work was the optimization of the test procedure for the hydrogen diffusion concerning reproducibility. For this purpose, two different lubricants BO318 and PFPE were tested by measuring the hydrogen permeation flow through a steel membrane using the electrochemical Devanathan and Stachurski technique. The following points summarize the results.

- 1. A reproducibility of the tests with BO318 oil was not achieved due to inhomogeneous palladium coating, inconstant oil volume, and due to high residual current.
- The measurements with the PFPE oil also proved not to be reproducible at first. By drying the filter paper, shortening the pre-treatment of the steel foil, and achieving a small residual current, a reproducibility of the measured values could be guaranteed.
- 3. The coating of the steel foil with palladium using the PVD technique was unsuccessful because the palladium layer with a thickness of 1nm exhibits pores and inhomogeneity.
- 4. A more accurate current is measured by purging the output cell with N₂. This interrupts the diffusion process of hydrogen, which is generated at the counter electrode of the output cell and detected at the WE.

The next step would be the exact investigation of the measured current as a function of the pressure of the introduced nitrogen. However, this approach has a limitation, since by purging the output cell with nitrogen, the solution is stirred as a side effect. No matter how much the pressure might get increased, a residual current will be always detected because of the stirring. For further experiments the development of a new set-up with the separation of the counter electrode from the output cell is necessary. The whole cell should be heated evenly. In addition the volume of the lubricant should be well defined, stable and adjustable. The next focus would be the simulation of the phenomena in a ball bearing at the steel-lubricant contact.

6. Lists

6.1. List of Reference

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7. Appendix



Appendix 1 Results with the PFPE oil without drying the filter paper M. monev and L. Mirkova from IPC, BAS, Sofia



Appendix 2 Measurement of the temperature in the input cell using an uncoated steel foil



Appendix 3 Comparison between steel foils coated with palladium by PVD (left sample) and by electroplating (right sample). On the right picture the palladium coating by PVD is removed with a tissue



Appendix 4 Boxplots of the data measured after five hours. Test series with PFPE oil: A – Steel WE with non-dried filter paper; B – Steel WE with dried filter paper; C – Pd WE with dried filter paper

| Test series | N total | Mean | Standard deviation | Min | Median | Max |
|-------------|---------|------|--------------------|------|--------|------|
| А | 5 | 0.54 | 0.11 | 0.42 | 0.56 | 0.65 |
| В | 16 | 0.45 | 0.12 | 0.26 | 0.7 | 0.60 |
| С | 8 | 0.49 | 0.07 | 0.35 | 0.5 | 0.58 |

Appendix 5 Statistic values obtained by the boxplot diagrams