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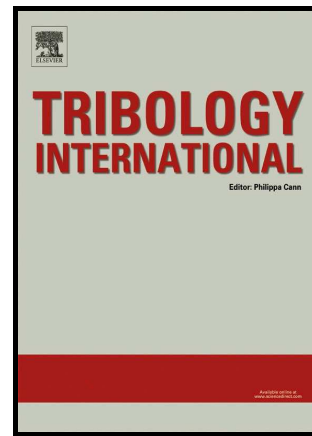


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## Author's Accepted Manuscript

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## Development of a novel *in-situ* technique for hydrogen uptake evaluation from a lubricated tribocontact

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### Abstract

Hydrogen in mechanical elements can be generated as a result of tribochemical reactions during surface-rubbing causing steel embrittlement. In this study, a new modified Devanathan-Stachurski setup in which a tribological charging cell is incorporated was developed in order to provide an online measurement of hydrogen permeation through steel from a lubricated metal-metal contact. This new technique enables the study of the hydrogen source and the rate of its permeation in a tribocontact. The effect of water contamination and the presence of conventional anti-wear and friction modifier additives in polyalphaolefin base oil on tribologically-induced hydrogen uptake were investigated. The results indicate significant influence of water on hydrogen uptake. The ZDDP anti-wear has promoted hydrogen uptake from the tribocontact. Whilst MoDTC friction modifier reduced the hydrogen permeation.

**Keywords:** Tribological hydrogen uptake; *In-situ* measurement; Electrochemical method; Oil decomposition

### 1. Introduction

Steels are widely utilised in many industrial applications due to their suitable mechanical properties, good performance, and reasonable cost [1]. However, hydrogen has been shown to have many deleterious effects on the mechanical properties of the steel. Steel alloys are susceptible to a loss in steel ductility and premature failure at lower stress concentrations in the presence of hydrogen. It has been demonstrated by several investigators that the steel fatigue life significantly shortens due to the presence of hydrogen [2-6]. Hydrogen atoms can easily penetrate into the steel due to their extremely small size. Therefore, damage of

metals due to hydrogen is prevalent and cannot be easily monitored and quantified which makes it even more catastrophic [7]

It has been stated that hydrogen is involved in some main issues of tribological components by promoting surface cracks and accelerating fatigue failure as well as micropitting [8]. Generally, micropitting is a form of wear process associated with tangential shear stress in a rolling-sliding contact. In the early stages, numerous microcracks initiate at, or very close to, the surface. These shallowly-inclined cracks propagate into the material in the direction opposed to that of the surface traction and eventually rupture occurs to form shallow micropits. Plastic deformation and fatigue cracking were seen during this type of failure [9]. Hoeprich [8] reported that hydrogen could increase the rate of microcrack/pit development on the metal surface and it is considered as a mechanism of surface initiated rolling contact fatigue. He concluded that hydrogen diffusion from the lubricant is a possible reason for the dark etching effect in gears. It was hypothesised that hydrogen diffusion into the steel happened as a result of tribological reactions at asperity contacts [8].

Atomic hydrogen which is generated as a by-product of oil decomposition can interact with steel to induce subcritical crack growth under the action of stresses leading to a decrease in material ductility. This will cause serious problems in critical components such as bearings [4-6, 10-16]. Uyama *et al.* [6] and Ciruna *et al.* [3] observed that hydrogen content in the AISI 52100 bearing steel is one of the prime reasons for reduced bearing life. They found that fatigue life of AISI 52100 bearing steel ball is inversely related to the hydrogen content in the steel. They correlated the reduction of fatigue life of the bearing steel (from  $10^6$  to  $10^3$  revolutions) with presence of 4 ppm hydrogen in the steel. Uyama *et al.* [6] proved that increasing hydrogen content in the steel from 0.03 mass-ppm to 1.2 mass-ppm, decreases steel fatigue life more than one order of magnitude. They pointed out that the shorter life of hydrogen-charged samples is due to the acceleration of the localised microstructural changes under rolling contact fatigue tests. The same behaviour has been reported as a result of hydrogen generation from grease decomposition [11].

It has been reported that environmental factors such as lubricant composition and tribological parameters influence the lubricant decomposition and hydrogen generation rate on the metal surface. Various hypotheses have been proposed to

explain the phenomenon; but the mechanism of failure is complex and a conclusive theory is yet to be established [17-20]. Moreover, the question “what is the main contributing factor to hydrogen generation from a lubricated contact?” has not been answered yet. Development of monitoring techniques, especially *in-situ* and real time, are important to follow the hydrogen generation process and its diffusion through the steel in a dynamic tribological system. It helps to identify tribochemical hydrogen uptake which is important for understanding the mechanism, assessing the risks, predicting the failure, and providing protective solutions.

Special efforts have been made so far regarding *in-situ* monitoring of tribological hydrogen gas evolution [5, 14, 16, 21]. In these research works, quadrupole mass spectrometer techniques were used in high vacuum or in a controlled gaseous atmosphere to analyse the products from tribochemical reactions occurring on the rubbing surface [5, 14, 16]. Lu *et al.* [14] investigated the effect of different additives on oil decomposition under friction conditions. They showed that phosphate-containing ionic liquid additives are more efficient in preventing the decomposition of lubricants in comparison with additives containing sulphur, nitrogen and phosphorus. Moreover, the study showed that phosphate-containing ionic liquid additives are more effective in increasing the critical load for hydrogen generation compared to other mentioned additives due to the higher durability of the tribofilm. However, the results of these experiments in such controlled atmospheres often miss some critical aspects of hydrogen generation and permeation if they are used to study the hydrogen embrittlement phenomenon. Firstly, one of the sources of hydrogen is believed to be attributed to oxidative decomposition of the lubricant on the fresh metal surface [14, 16], but doing the experiment in a vacuum chamber delays the oxidation of fresh surface and increases the hydrogen generation compared to real working condition. Secondly, these techniques only detect non-absorbed hydrogen. However, tribological contacts introduce significant quantity of hydrogen into the contacting bodies and indeed what matters most in terms of hydrogen embrittlement is hydrogen permeation into the steel and not hydrogen gas evolution.

Considering the limitations of the previous *in-situ* measurements, modifying the Devanathan-Stachurski (DS) setup has been chosen in the current study in order to develop a new technique to monitor hydrogen uptake into the steel from a lubricated tribological contact. The conventional DS technique [22] is used extensively in the

investigation of hydrogen permeation flux through a thin steel membrane under a wide variety of conditions. The high sensitivity of electrochemical techniques used in DS method allows very detailed real-time measurements to be taken; any slight change of the hydrogen evolution rate on entry side can be reflected in the hydrogen permeation current.

Many types of modified DS cells were applied to investigate hydrogen permeation through the steel with different hydrogen entry conditions. Turnbull *et al.* [23] reported that addition of H<sub>2</sub>S and decreasing pH in entry electrolyte would increase the hydrogen entry. Tsuru *et al.* [24] modified a DS set-up to study the mechanism of hydrogen entry into the steel during an atmospheric corrosion process and the effect of the steel passive layer and surface pH on the permeation rate. Ootsuka *et al.* [25] later used the developed technique by Tsuru *et al.* [24] in order to do online monitoring of hydrogen absorption into steel parts of a vehicle.

Despite all investigations into the effect of hydrogen on tribological fatigue related failures, it still remains unpredictable, difficult to control, and the complete mechanism is unknown. The detailed process and the influential parameters are also not well understood. This work has been motivated by the study of the influence of lubricant's composition on hydrogen entry into the steel. The objectives of this work are to (1) develop an *in-situ* technique for evaluation of hydrogen uptake from a lubricated tribocontact, (2) investigate the effect of water contamination and two commonly used lubricant additives on hydrogen permeation into the steel.

## **2. Design and development of the hydrogen uptake rig**

### **2.1. Design requirements**

In the conventional DS technique [22], the front and back sides of a metal membrane are exposed to two separate environments and employed as hydrogen entry and exit electrodes, respectively. The schematic figure of a conventional DS setup is shown in Fig. 1. In the hydrogen input side, hydrogen atoms produce and penetrate into the steel membrane by diffusion, while the amount of hydrogen diffusion is measured by the oxidizing current density in the detection side. Efforts have been put into the standardisation of the hydrogen permeation experimental procedures; thus, the BS EN ISO 17081 (2014) [26], method of measurement of hydrogen permeation and

determination of hydrogen uptake and transport in metals by an electrochemical technique, was accepted as the standard method of doing the experiment.

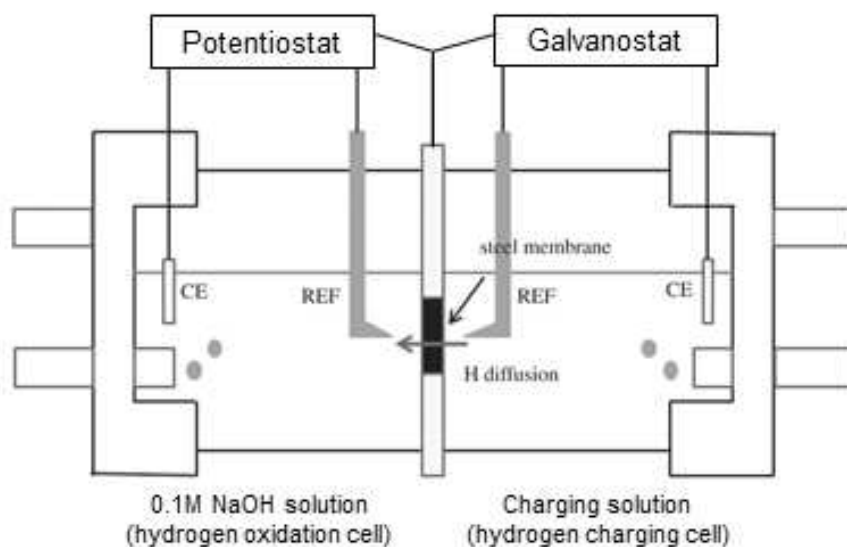


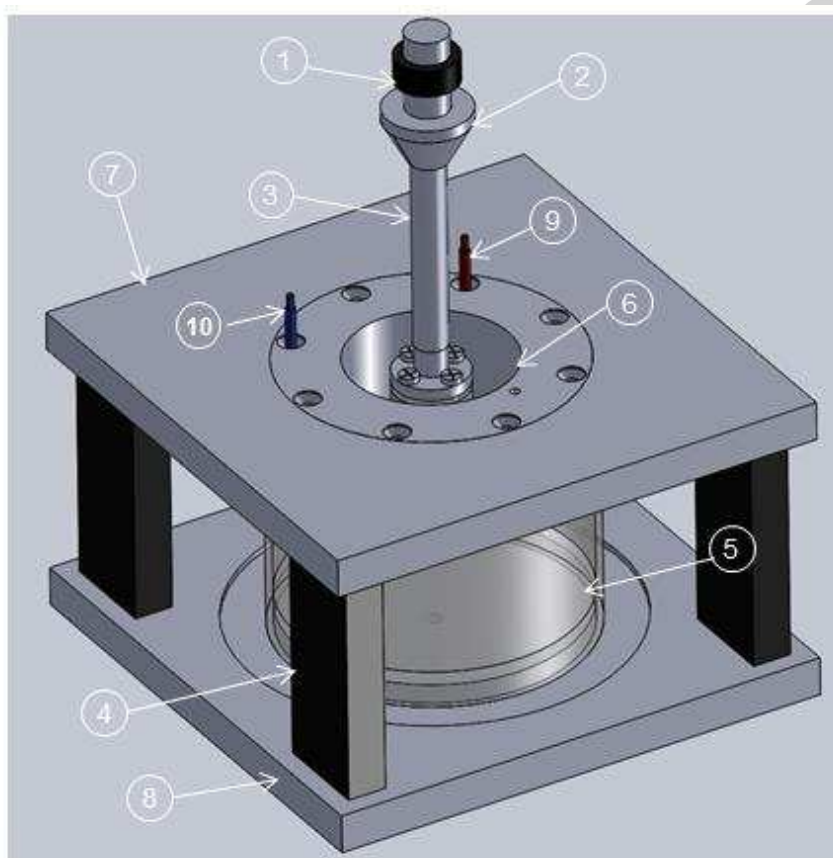
Figure 1: Schematic of conventional Devanathan-Stachurski cell, REF – reference electrode, CE – counter electrode

However, in the modified setup developed in this study, the charging cell is replaced by a tribocontact. The tribocontact imposes a highly stable thrust load and shear stress with low vibration, no misalignment, and long-time running accuracy. This is built in order to generate hydrogen on the charging side of the membrane to study the performance of candidate oils under different loads and sliding speeds. The load distribution, torque, and hydrogen oxidation current are continuously monitored during the test. Applied load and frequency of reciprocating rotation are adjustable in order to evaluate the dependence of hydrogen uptake on the variation of tribo-mechanical action. This technique will provide new insight into how both the lubricant's chemical and tribological parameters influence hydrogen uptake into the steel.

## 2.2. Hydrogen uptake rig

In this new rig, a vertical configuration has been designed and built having the detection cell beneath and applying the load from top. The detection cell made of glass is working similar to the conventional DS setup. However, the hydrogen charging cell has been replaced by a lubricated sliding contact. Schematic diagram of the test apparatus used in this study is shown in Fig. 2. In this technique, the load

is applied from the top using a shaft held by chuck via a linear motion derived by pneumatic pump. The rotational motion is also introduced by pneumatic force using an Instron E10000 machine with variable speeds; the entire instrument is computer controlled. The flat metal ring (Fig. 3) with rough running surface which is fixed on the bottom of the shaft is loaded against the membrane and is reciprocating sliding on the membrane surface. The membrane is fastened and sealed on bottom of the oil bath between a clamp and detection cell. An area of  $3.5 \text{ cm}^2$  was exposed to the electrolyte inside the detection cell. The applied load and driving torque are recorded continuously during the experiment by using a Dynacell™ load cell. In this technique, hydrogen is produced on the oil side of the membrane and some of this hydrogen, the proportion is unknown, permeates within the steel membrane.



- |                             |                         |
|-----------------------------|-------------------------|
| 1. Load cell                | 6. Oil bath             |
| 2. Chuck                    | 7. Top plate            |
| 3. Shaft                    | 8. Base plate           |
| 4. Pillars to bear the load | 9. Counter electrode    |
| 5. Detection cell           | 10. Reference Electrode |

Figure 2: Isometric schematic view of hydrogen uptake setup



The tribological contact in this set-up is made of the membrane surface and a rubbing counterpart. The rubbing counterpart for this work is a cylindrically shaped sample drilled with a 7 mm inner diameter hole; the outer diameter is 18 mm, providing 215.9 mm<sup>2</sup> contact area of the bottom flat surface with the membrane (Fig. 3). The counterpart is made of stainless steel 303, chemical composition is shown in Table 1. The running surfaces of the specimens were roughened to an average roughness  $R_a=12\ \mu\text{m}$ . This tribological contact is not an exact representation of a common tribology regime for rolling contact fatigue evaluation; however this sliding contact provides shear stress and wear which are essential for hydrogen generation from a lubricated contact.

Table 1: Chemical composition of stainless steel 303 in wt%

C	Cr	Ni	P	S	Si	Mn	Fe
max 0.15	18	8	max 0.2	max 0.15	max 1	max 2	Balance

The thrust load and shear stress between the membrane surface and the rubbing counterpart were estimated to be high enough to produce wear and remove the surface oxides, decompose the lubricant and produce enough hydrogen to diffuse into the steel membrane.

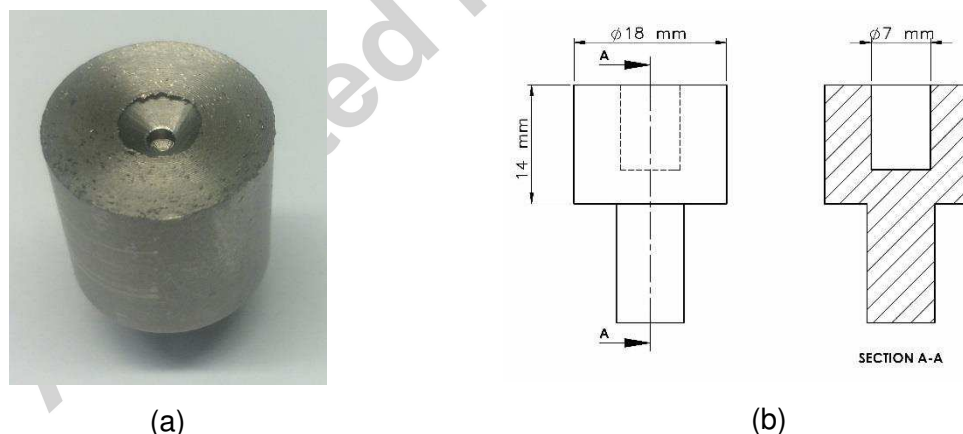


Figure 3: (a) The flat ring used as rubbing counterpart; (b) 2D drawing of the rubbing counterpart and dimensions

A self-aligning mechanism was implemented in the shaft in order to keep the rubbing counterpart aligned with the membrane surface during rotation. As shown in Fig. 4, a hemisphere between two plates and loose pins corrects the misalignment between the bottom of the rubbing counterpart and the membrane surface; this is important as

it assures to have a uniform load distribution in rubbing area. This mechanism is able to transfer both load and torque from the shaft to the rubbing counterpart.

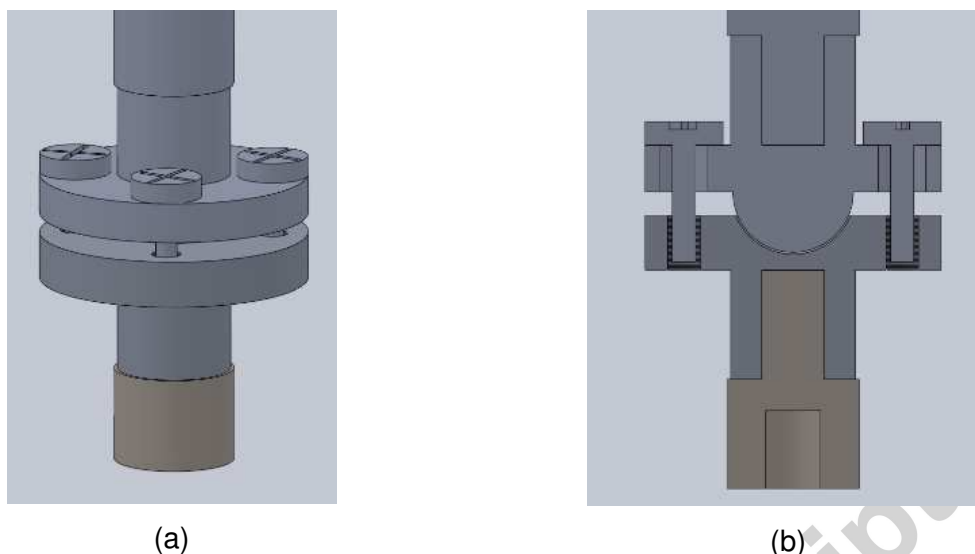


Figure 4: (a) Schematic and (b) cross section view of self-aligning mechanism

### 2.3. Electrolytic cell and procedure

In the current work, the hydrogen detection cell is the same as in a conventional DS cell. It is made up of a three-electrode system with the steel membrane as the working electrode, platinum wire as the counter electrode and Ag/AgCl as the reference electrode. The cell was filled with a deaerated solution of 0.1 M NaOH. The detection side was polarized at a constant potential of 115 mV versus reference electrode which is sufficient to oxidise the hydrogen atoms emerging on the output face. This anodic potential is maintained on the detection side and the hydrogen leaving the membrane is removed by oxidation according to Eq. (1) until the current becomes very small.



Once the background current density was stabilised and it reached under 250 nA/cm<sup>2</sup>, which is a low background compared to the measured current density, the oil bath (hydrogen input side) was filled with 75ml of the oil of interest. Then the load was applied and rubbing started; the metal counterpart is rubbing against the membrane surface under reciprocating sliding condition. All the tests were identical and were conducted under the operating conditions described in Table 2. The only difference in the tests was different lubricants used to fill the oil bath. Information on the oils used in this study is shown in Table 3.

Table 2: Operating parameters

Kinematics	Reciprocating sliding (rotational move between two flat surfaces)
Load	70 N
Angular displacement amplitude	55 deg.
Frequency	1 Hz
Test duration	5 h

The hydrogen atoms which permeated through the steel membrane during rubbing were oxidized by the applied anodic potential and the oxidation current was continuously measured with data logging every 10 seconds. The hydrogen oxidation current is recorded by using an Ivium potentiostat linked to a computer for data capturing and used to quantify hydrogen permeated through the steel. All experiments were carried out at room temperature which was  $25\pm 2^\circ\text{C}$ . All measurements were performed at least two times to assure reproducibility. At the end of the test, the specimen was removed, ultrasonically cleaned with heptane and used for surface analysis.

Table 3: List of oils

Code	Lubricant	Description
A	PAO	Polyalphaolefin high purity, synthetic, non-polar base oil
B	PAO+water	5% water - emulsified
C	PAO+salt water	5% salt water (3.5% NaCl) - emulsified
D	PAO+ZDDP	0.08% P
E	PAO+ZDDP+MoDTC	Lubricant D + 1 %wt MoDTC
F	PFPE	Perfluoropolyether

#### 2.4. Sample preparation and materials

The hydrogen uptake behaviour of the AISI 52100 steel was investigated using the new modified DS rig described in section 2.2. The chemical composition of the steel membrane is shown in Table 4. The specimens were discs of about 0.8 mm thickness and 40 mm diameter. Both sides of the specimens were ground up to 1000 grit paper. The specimens were cleaned and then dried in oven. The cleaning process was done by ultrasonic immersion of the specimens in ethanol and then the detection sides of the membranes were coated with a 40 nm thick palladium coating, applied by sputter coating method.

Table 4: Chemical composition of AISI 52100 steel in wt%

C	Mn	P	S	Si	Cr	Fe
0.95-1.10	0.25-0.45	0.025	0.025	0.15-0.35	1.35-1.65	Balance

All the hydrogen atoms leaving the steel membrane to the detection side need to be oxidised. However, some of these atoms could recombine to hydrogen molecules before getting oxidized. This amount of hydrogen escapes and is not measured by the oxidation current recorded at the detection side. Partial oxidation of hydrogen atoms could compromise the reliability of the method. The palladium layer on the detection side significantly reduces this unmeasured fraction of hydrogen and ensures high detection efficiency and minimized noise levels [27-29]. Another advantage of having a thin layer of palladium is that it prevents anodic dissolution of the metal membrane, otherwise an oxide layer would form on the metal surface which acts as a diffusion barrier for hydrogen [27, 28, 30].

## 2.5. Wear measurement and data analysis

After the tests, the membranes were rinsed with heptane in an ultrasonic bath and then examined by white light interferometry in order to study the profile of the wear track. Two and three-dimensional images were taken from four different areas of the wear track on each sample and the average wear width and depth of different areas were calculated. The average wear width and wear depth were used to estimate wear volume of each sample. Fig. 5 shows an example of wear measurement image using white light interferometry. The average wear depth was measured by comparing the average heights of points inside and outside of the wear track as shown in Fig. 5-c.

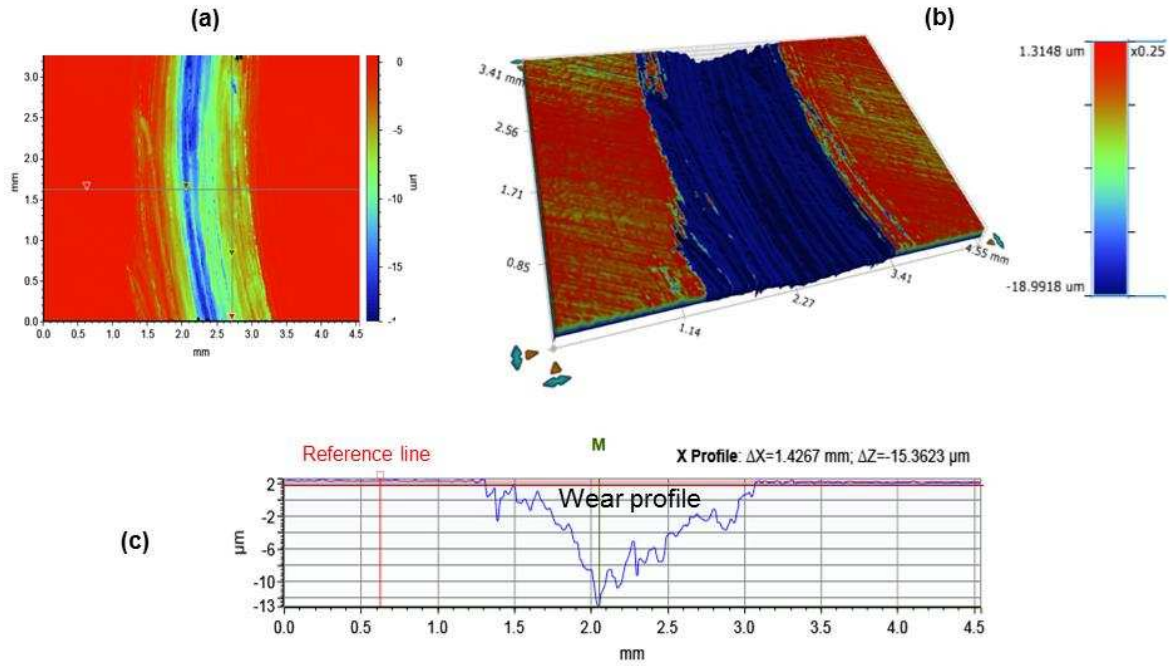


Figure 5: (a) Two dimensional and (b) three dimensional images of wear track (c) image profile of the membrane surface after the experiment

The amount of permeated hydrogen through the steel per second,  $S$  ( $\text{mol}/\text{cm}^2\text{s}$ ), can be estimated by integrating hydrogen permeation current density with time by using the following equation [25]:

$$S = \frac{1}{Ft} \int_0^t I dt \quad (2)$$

Where  $I$  is hydrogen oxidation current density ( $\text{A}/\text{cm}^2$ ),  $F$  is Faraday's constant ( $96,485 \text{ C}/\text{mol}$ ) and  $t$  is the integration time (s).

### 3. Results and discussion

#### 3.1. The source of hydrogen in a lubricated tribocontact

After mounting the sample and applying the constant anodic potential on the detection side, the whole unit was left to reach steady state overnight, without applying the load, producing a decay current curve as shown in Fig. 6. Once the current ramped down, the oil bath was filled, the load was applied and rubbing started.

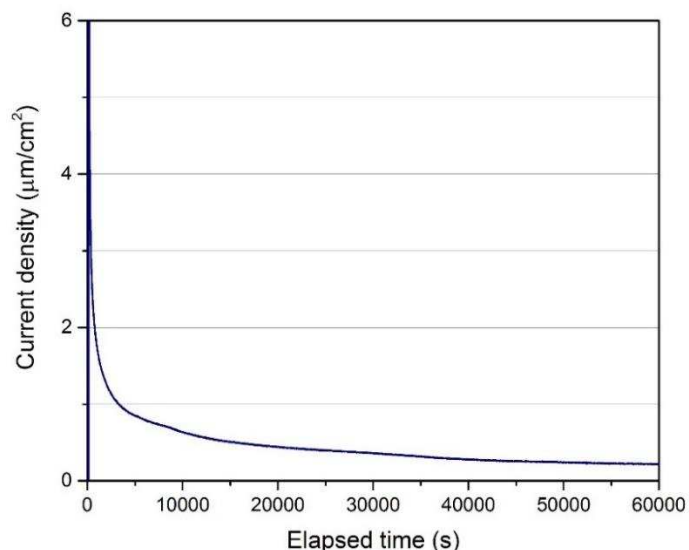
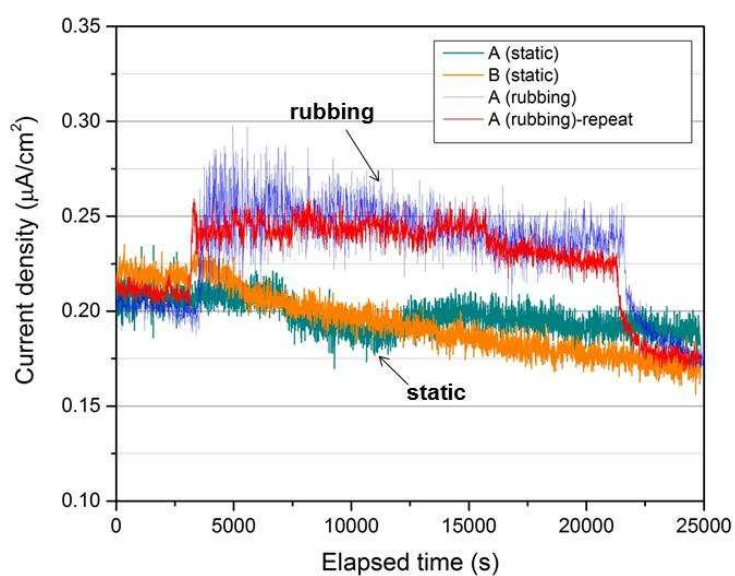


Figure 6: Current decay curve

Initially, some experiments were done in order to assess the effect of rubbing on hydrogen permeation into the steel. The results from static experiments in Fig. 7(a) show the effect of pure corrosion reactions on hydrogen permeation rate into the steel. The lubricants were the same as the ones used for the other hydrogen uptake measurements, but without rubbing the metal surface. Although corrosion products were clearly observed on the membrane surface after the experiment, as shown in optical image in Figs 7(b), the permeation results show no increase in permeation current in absence of sliding on the charging side of the membrane. The same behaviour was seen for other lubricants (C, D and E).

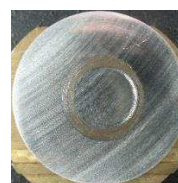


(a)



Lubricant B (static)

(b)



Lubricant A (rubbing)

(c)

Figure 7: (a) The effect of rubbing on hydrogen permeation; (b), (c) optical images of the worn surface after the experiment

The increased permeation current during rubbing of the lubricant A, shown in Fig. 7(a), indicates that hydrogen can be generated from PAO base oil. The obtained hydrogen uptake curves in this study are similar to the typical curves from conventional hydrogen permeation experiments [31]. Fig. 8 shows the form of the hydrogen permeation data which is presented as a plot of current against time. The key components of this current versus time plot are:

- I. A stable and static current in static conditions
- II. An induction time when rubbing starts after which current rises
- III. The current remains high either at a steady state or decreasing depending on conditions; this is discussed later
- IV. A decay of current when rubbing stops.

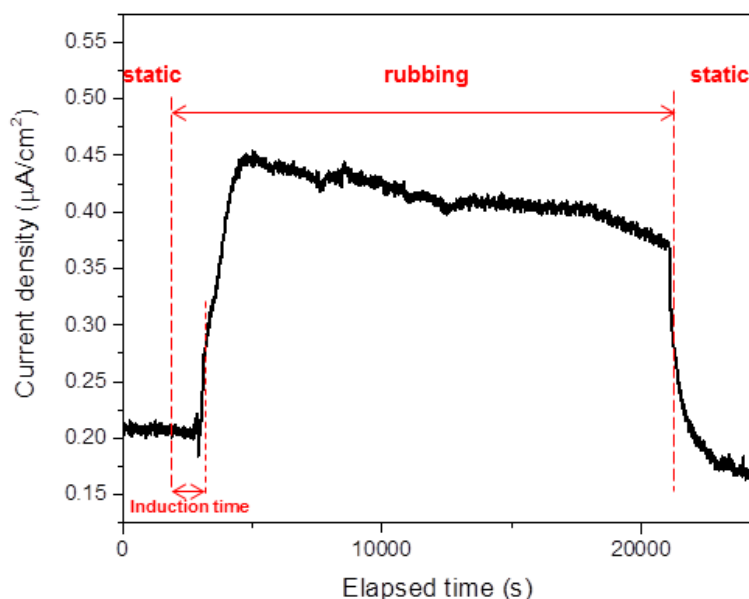


Figure 8: Typical hydrogen permeation charging and de-charging curve

Comparing the hydrogen permeation results from static and under rubbing conditions in Fig. 7(a), it is revealed that hydrogen permeation is occurring primarily as a result of tribological processes and not as a result of surface oxidation. This is in line with previous *in-situ* measurements that showed emitted hydrogen from tribological contact only happens when sliding occurs on the surface [5, 16]. It has also been revealed that lubricant decomposition rate is directly related to sliding velocity and the applied load [13, 14, 16]. Molecular dynamics simulations [12] have also shown

that if a lubricant film is subjected to shearing between two sliding surfaces, both hydrogen diffusion and hydrogen adsorption on the metal surfaces will be induced. Moreover, starting and stopping the rubbing (Figs. 7(a), 11(a) and 12(a)) confirm that the production of hydrogen is tied to the rubbing process. The surface rubbing forms nascent steel surface with active sites by removing contaminants and surface oxide layer. The fresh metal surface catalysis oil decomposition process. The presence of shear stress in tribological tests also promotes lubricant decomposition through rupturing of bonds [21].

In this experiment, hydrogen is produced on the rubbing side of the specimen and its concentration becomes stable in a short time. On the other hand, the concentration of hydrogen atoms on the detection side of the specimen remains negligible throughout the experiment due to applying oxidizing conditions. Therefore, hydrogen is permeated through the sample as a result of the hydrogen concentration gradient between two sides of the steel sample. The induction time takes for hydrogen atoms to emerge on the detection side of the sample depends on the thickness of the specimen. The steady state current value and the time needed to reach steady state depend on the concentration of hydrogen on the rubbing side as well as the steel microstructure which determines hydrogen diffusivity.

In order to verify the origin of the hydrogen, a control test was done by using hydrogen free lubricant, perfluoropolyether known as PFPE. PEPE is a nontoxic, long chain polymer consisting carbon, oxygen and fluorine atoms in its structure. The PFPE mechanism of lubricating is mainly related to its outer layer of non-reactive fluorine atoms. This causes the adjacent molecules to easily slip by each other allowing the formation of a PFPE film layer formation on the surface. This film is efficient in reducing wear and minimising friction. However, the main reason for choosing PFPE for control test in this study is the fact that it does not have hydrogen in its structure, unlike hydrocarbon lubricants. Therefore, no hydrogen permeation increase is expected with having PFPE as lubricant. As shown in Fig. 9, when rubbing is started in the PFPE fluid as lubricant no hydrogen permeation current is observed apart from an offset in decay baseline. The curve shape is different from hydrogen permeation curve that gradually increases and reaches a steady state.



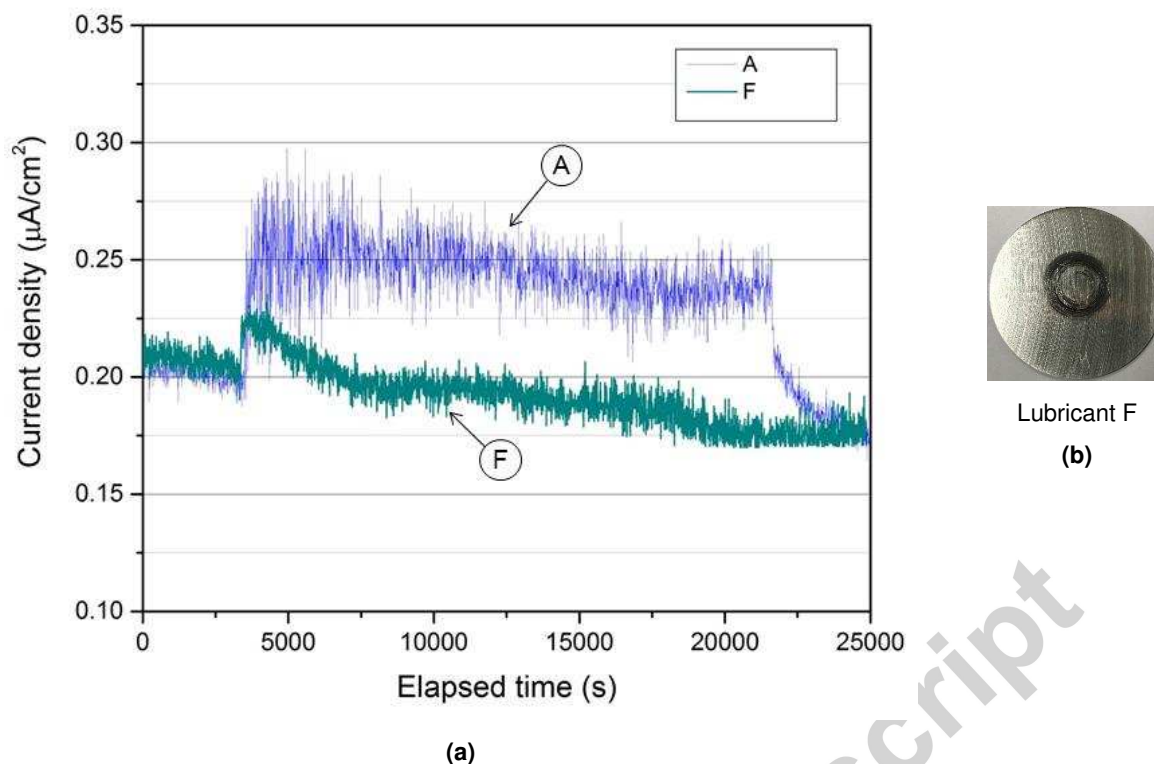


Figure 9: (a) The comparison between lubricant F (PFPE) and lubricant A (PAO) in promoting hydrogen permeation (b) optical image of the worn surface after the experiment

Considering the obtained results for PFPE lubricant, the hydrogen evolution from the lubricated contact in Fig. 7(a) is suggested to come mainly from hydrocarbon lubricant's decomposition [3, 14, 16]. It has been suggested that oils composed of hydrocarbons decompose under repeated stress and heat caused by rubbing contact and generate hydrogen. This hydrogen diffuses into the steel and exceeds the critical value, causes shorter rolling contact fatigue life [4]. Thermal decomposition of chemisorbed water and surface contaminants participating in the tribochemical processes occurring at the interface are the other possible sources of hydrogen evolution [10, 14, 16].

The lubricant film in the asperity contact is subjected to high temperature, pressure, and friction which can cause lubricant decomposition and hydrogen generation [21, 32]. It is also assumed that the nascent steel surface formed due to the removal of metal oxides and organic contaminants under mechanical stimulation condition catalyses decomposition reaction of organic materials. The decomposition of lubricant molecules accelerates not only by high activity of fresh metal surface, but also by some other parameters such as high local temperature of the contact

surfaces, shear stresses on sliding surface and pressure at the contact area [3-5, 13, 14, 16, 33].

There is a proposed mechanism describing oil decomposition and tribochemical reactions occurring during tribocontact [16, 21]. According to this scenario, hydrocarbon oil initially adsorbs on nascent surfaces which are generated by mechanical contact. This is followed by C-C bond rupture which leads to production of lighter hydrocarbon by unzipping of the molecular chain. As a result of this process, hydrogen is formed and the metal surface is covered by  $C_xH_x$  species through iron-carbon bonds. These organic deposits will be removed later by friction forces and the whole process repeats again. The material defects on the fresh steel surface generated through wear processes as well as the high temperature at the contact are necessary to promote the decomposition of the oil. Another possible mechanism to consider is the formation of lighter oil molecules through the shear-induced breakdown of the long hydrocarbon chain [16, 21]. Fig. 10 shows the proposed reaction pathway for decomposition of hydrocarbon oil initiated by nascent steel surface formation.

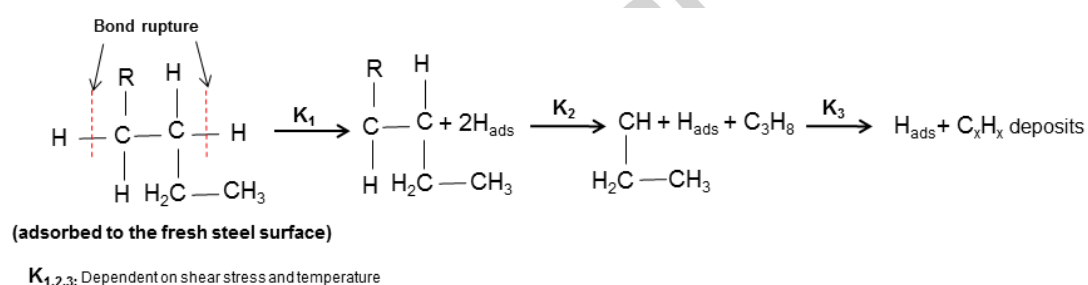


Figure 10: Proposed reaction pathway for decomposition of hydrocarbon oil within tribocontacts [16, 21]

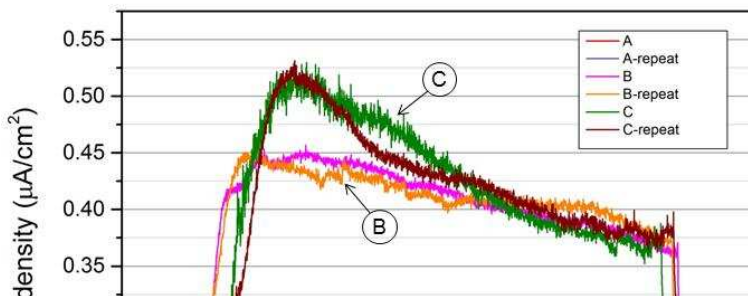
It should also be noted that some of the generated hydrogen diffuses into the rubbing counterpart. However, hydrogen atoms are prone to diffuse towards tensile stress fields [34, 35]. Therefore, more hydrogen diffuses into the membrane when its surface is loaded and hydrogen transportation into the subsurface material is enhanced under compressive stresses [32].

### 3.2. The effect of water contamination on hydrogen permeation

Water contamination in oil is considered as one of the prime sources of hydrogen in a lubricated tribosystem. Water promotes hydrogen generation through the reduction

of its molecules on the fresh metal surface and also by accelerating oxidative decomposition of the lubricant [3]. The water enters the lubricating oil during operation of the bearing either from humid air in contact with the lubricant or condensation of the water in the system. Deleterious effects of water contamination on the bearing fatigue life have been widely investigated so far [3, 36-40]. Even a very small amount of water (20 ppm) is known to accelerate fatigue failure of steel. Grunberg and Scott [41] showed that 0.002 percent water content reduced the surface fatigue life of steel to 48 percent. Cantley [36] has shown that presence of water in oil significantly lowers bearing fatigue life and this effect increases in higher water concentrations. Referring to his results, water absorbing capacity of oil varies according to chemical composition and additives of the oil. Gao *et al.* [42] reported that presence of water changes the mechanism of rolling contact fatigue failure from spall-related failure into crack-related failure. Schatzberg and Felsen [37, 38] have concluded that increasing water content from less than 10ppm to 100ppm in lubricant causes 43 percent reduction in fatigue life at 9 GPa stress level. Similarly, for the same variation in water content, 48 percent reduction in fatigue life was observed at 7.6 GPa cyclic stresses.

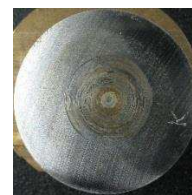
Results presented in Fig. 11(a) show the changes in hydrogen permeation current during rubbing using lubricants A, B and C to fill the oil bath. The water in lubricants B and C exceeded its saturation level in the oil and so was suspended as microscopic droplets. For these tests, there was a visible cloud or haze in the oil. The water-oil emulsion mixture was prepared by injection of water into the oil and putting the container in an ultrasonic bath for 15 minutes.



Lubricant B

(b)

(a)



Lubricant C

(c)

Figure 11: (a) The effect of water contamination on hydrogen permeation current; (b), (c) optical images of the worn surface after the experiment

From Fig. 11(a), it can be observed that the hydrogen oxidation current incrementally increases after a certain time lag corresponding to the hydrogen travelling time across the steel when the sliding was started which means that hydrogen was evolved as soon as friction was commenced [24]. It indicates that oxidation current increase occurs as a result of higher hydrogen diffusion and chemical reactions at the interface due to friction rubbing. Fig. 11(a) shows that once the sliding process was terminated, the permeation current returned gradually to the initial value within several minutes.

Fig. 11(a) shows that the hydrogen permeation current in the presence of water in lubricant was significantly higher compared to lubricant A which is free from water contamination. The significantly higher hydrogen permeation in presence of water can be due to the formation of hydrogen as a product of surface corrosion reactions occurring on the metal surface [37, 38]. Another observation about lubricants B and C (containing water and salt water, respectively) is that the current density does not reach steady state. This appears to be a result of non-uniform generation of hydrogen over the charging surface due to the highly corrosive system. It could also happen due to the formation of corrosion products on the surface which hinders further permeation of the hydrogen atoms. The surface oxides are visible on the surface of the samples examined in oils with water mixture (Figs. 11(b) and 11(c)). Schatzberg and Felsen [37, 38] have reported occurrence of corrosive wear in a lubricated rubbing interface with having water as contamination. The permeation current for lubricants B and C showed a maximum around 1h and 1.5h, respectively, after the start of rubbing and then start to decrease. Progressive accumulation of corrosion products and deactivation of the surface could lead to the decrease in hydrogen formation from the tribological interface. In other words, the permeation current steady state is not achieved as the formation rate of nascent surface which is

related to the sliding velocity do not balance with the diminishing rate of active sites with corrosion products covering the surface.

According to the suggested mechanism associated with the effect of water on fatigue life of the bearing, water could decrease fatigue life in two ways. Firstly, water causes corrosion on the metal surface and forms additional surface defects such as micropits which act as significant stress raisers. Surface cracks could originate from these defects at lower stresses and propagate until material failure. Gao *et al.* [42] have revealed that cracks are formed more readily and in greater numbers in water-lubricated contacts compared to oil-lubricated contacts. Secondly, once cracks have formed, water could squeeze into the crack by the passing load and forced ahead of the surface microcrack. It has been suggested that the water reacts with the fresh metal surface at the crack tip. It can be expected, therefore, that water breaks down generating hydrogen. This hydrogen reduces mechanical strength of the steel as a result of hydrogen embrittlement and causes higher crack growth rate [37, 38, 40]. It is hard to obtain continuous observation of crack initiation and propagation; however the higher hydrogen permeation current in presence of water recorded in our experiments confirms the latter hypothesis. It should be noted that the magnitude of water effects depends on other factors such as load and operating temperature. Therefore, these results should be restricted to the conditions similar to the one employed in obtaining the test data.

### **3.3. The effect of lubricant additives on hydrogen permeation**

Some additives such as anti-wear and extreme pressure additives are known to promote micropitting [8, 9, 43-45]. In particular, Laine *et al.* [44] and Benyajati *et al.* [45] showed that the anti-wear additive, zinc dialkyldithiophosphate (ZDDP), causes micropitting to become more severe compared to a simple base stock. Spikes *et al.* [9] reported a nearly inverse relation between micropitting damage and the wear in sliding contacts for lubricants containing secondary ZDDP for various concentrations between 0-1.3 wt%.

Higher concentrations of hydrogen on the steel surface is also considered as one possible root for white etching area cracks formation. This is a type of rolling contact fatigue commonly seen as macropitting on bearing surfaces. Hydrogen embrittlement is believed to reduce the steel strength and promotes localised plastic

deformation. Therefore, white etching area cracks could happen and the mechanism is called hydrogen enhanced localized plasticity [46]. In order to have a better understanding about the ability of lubricant additives to affect the permeation of hydrogen, this new developed technique is employed to assess hydrogen transfer into the steel from a lubricated tribocontact in presence of different additives.

Curves in Fig. 12(a) compare the changes in hydrogen permeation current during rubbing with lubricants D and E as described in Table 3. The effect of lubricant additives on hydrogen permeation into the steel is shown in this figure and a good repeatability was seen in the results. Comparing Figs. 7(a) and 12(a), it is clear that ZDDP as an additive in the lubricant increases the measured hydrogen permeation current compared to the base oil. However, the measured permeation current is lower in presence of molybdenum bis-diethylhexyl dithio-carbamate (MoDTC) as an additive in the lubricant. The total amount of permeated hydrogen shown in Fig. 13 also clarifies the contradictory effect of these two lubricant additives on hydrogen uptake into the steel.

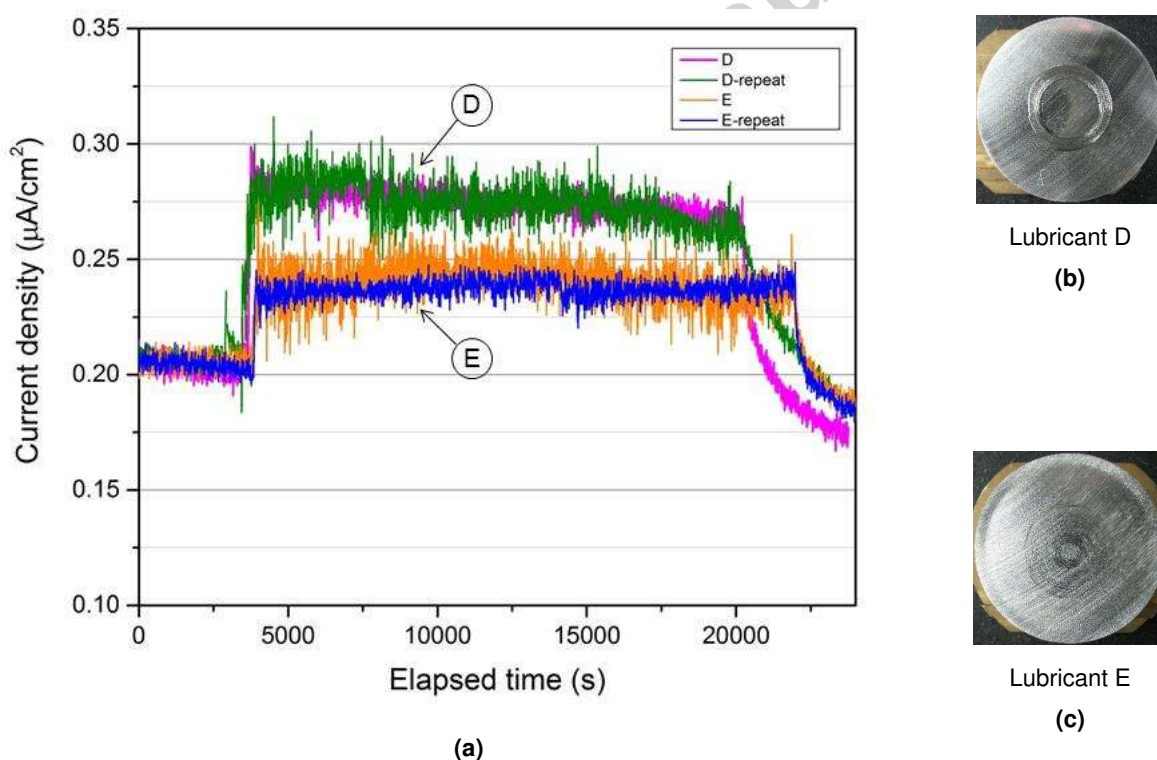


Figure 12: (a) The effect of lubricant additives on hydrogen permeation current; (b), (c) optical images of the worn surface after the experiment

Comparison of the curve A in Fig. 7(a) and curve D in Fig. 12(a) reveals that although ZDDP additive in the base oil acts as an anti-wear agent and decreases the

wear, it slightly increases the hydrogen penetration rate into the steel; this behaviour is also presented in Fig.13. This is consistent with previous experimental results obtained by other researchers that showed hydrogen diffusion into the steel is not reduced in presence of anti-wear additives [5]. The Higher permeation of hydrogen in presence of ZDDP is due to the fact that ZDDP decomposition products act as poisoning agents to inhibit the recombination of atomic hydrogen to hydrogen gas leading to an increase in the concentration of atomic hydrogen at the metal surface [47]. Consequently, the concentration gradient of hydrogen increases and hydrogen has more probability to diffuse into the steel before desorption from the surface as hydrogen gas.

On the other hand, another investigation by Laine *et al.* [48] showed that the presence of friction modifier additive (MoDTC) in a formulation consisting of a mineral base stock and ZDDP significantly decreased micropit formation compared to the lubricant consisting of ZDDP alone. The positive effect of friction modifier additive (MoDTC) on reducing hydrogen permeation into the steel is also seen in our experiments as shown in Fig. 13. The beneficial effect of MoDTC is postulated to be due to the reduced friction at asperity levels when lubricant E is used. The lower friction value for lubricant E is due to the MoS<sub>2</sub> deposition in asperity contact [49]. It also reduces the rate of nascent surface formation by reducing wear (Fig. 13) which is another reason for lower hydrogen generation during rubbing.

#### **3.4. Wear results in comparison with hydrogen permeation**

The total amount of hydrogen which is permeated into the steel membrane from tribocorrosion processes occurring on the metal surface is calculated using Eq. 2. The results are plotted in Fig. 13 versus the average wear volume for different lubricants. This figure includes changes in hydrogen permeation as a result of changes the lubricant type while operating conditions are kept constant. As it can be seen, the lubricant+additives/lubricant+water contamination has shown differences of a factor of four. This is an important observation as it shows how significant the effect of water contamination is in lubricant as a contributing factor in hydrogen generation from a lubricated tribological contact. In the MoDTC containing lubricant (lubricant E) the total adsorbed hydrogen was slightly lower than that in the PAO base oil (lubricant A); however in the lubricant which contains ZDDP (lubricant D) the

total permeated hydrogen is higher than the base oil. It is seen that the amount of hydrogen permeation into the steel in lubricant D is higher than that of lubricant A, although the wear volume in presence of ZDDP additive is lower than the wear in PAO base oil. This means that there is co-existence of chemical and physical mechanisms involve in promoting hydrogen uptake. More data is needed to confirm the link between the wear/tribological conditions and the hydrogen permeation rate.

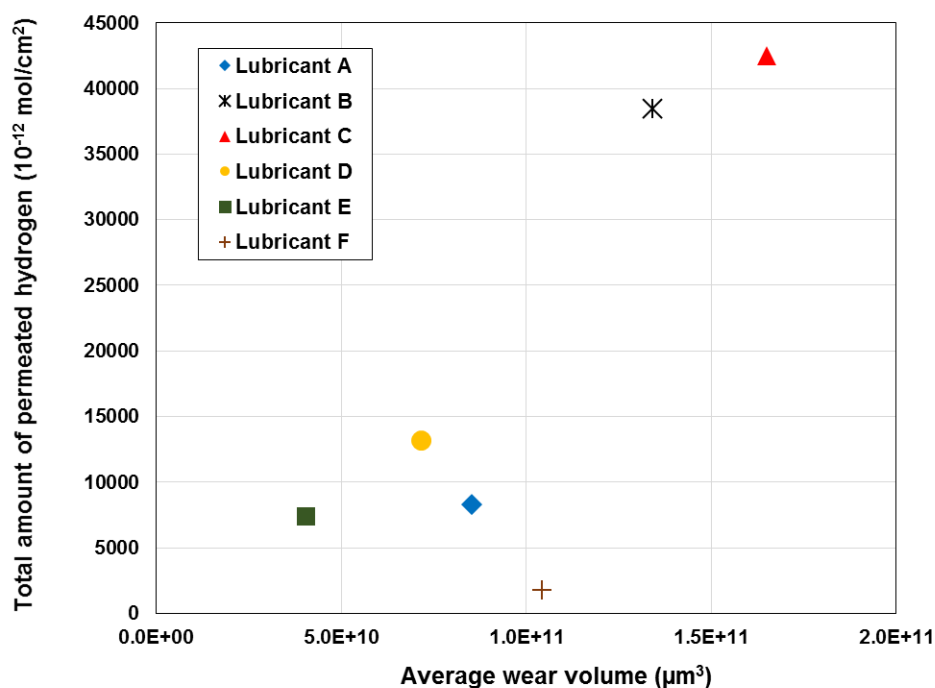


Figure 13: Wear volume in comparison with total permeated hydrogen through steel

#### 4. Conclusions

A novel method based on the modified Devanathan-Stachurski technique has been developed to experimentally assess hydrogen permeation into the steel from a metal-metal lubricated sliding contact. Reproducibility of the results was acceptable when precautions were taken to avoid contamination of surfaces and keep the palladium coating free from mechanical damage. The results indicate that the hydrogen permeation rate is strongly dependent on the lubrication type and condition. Under the conditions tested, the following conclusions can be drawn.

- (1) Hydrogen permeation was not detected in absence of sliding contact which shows hydrogen permeation happens as a result of tribochemical process in such setup.



- (2) Hydrogen uptake was not detected when hydrogen-free lubricant was used showing that the hydrocarbon base oil is one of the sources of hydrogen generation in a metal-metal lubricated contact.
- (3) It was shown that hydrogen uptake was substantially promoted in presence of water contamination in the lubricant. According to the results, it can be concluded that hydrogen uptake from the tribological contact into the steel increased up to four times higher in presence of 5% water mixed into the PAO base oil.
- (4) Hydrogen uptake is promoted in presence of anti-wear additive (ZDDP) in the lubricant. It is supposed to be due to the inhibition effect of ZDDP on the recombination of hydrogen atoms.
- (5) Hydrogen permeation decreases in presence of MoDTC additive in the lubricant; this is likely to be due to the reduced friction at asperity levels and lower rate of nascent surface formation because of lower friction and wear.
- (6) Both chemical and physical mechanisms are involved in promoting hydrogen uptake
- (7) The capability of this *in-situ* hydrogen uptake measurement rig was verified for different lubricants and the results are promising. More results and development of this new measurement technique will be reported in the future.

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**Highlights**

- Real-time monitoring of hydrogen permeation into the steel as a result of lubricated tribocontact
- Decomposition of hydrocarbon molecules is one of the sources of hydrogen in lubricated contacts
- The anti-wear additive in the base oil promotes hydrogen permeation into the steel
- The friction modifier additive in the base oil impeded hydrogen diffusion into the steel
- Water contamination in the oil significantly increases hydrogen permeation

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