

Tribology of PTFE in Hydrogen Atmosphere

Shouyi Yin , Ambrose Taylor, Janet S.S. Wong ^{*} 

Department of Mechanical Engineering, Imperial College London, London SW7 2AZ, United Kingdom

ARTICLE INFO

Keywords:

PTFE
Sealing materials
Hydrogen
Tribosystem reaction
Fretting

ABSTRACT

Hydrogen applications face sealing challenges. Often, these seals are made of PTFE and work under fretting conditions. Experiments in this study were conducted with PTFE against 52100 steel under varying humidity. Results show significant wear of PTFE in hydrogen, regardless of humidity, with PTFE transferring onto steel surfaces. FTIR and XPS analyses reveal that hydrogen's reducing effect suppresses surface metal oxide formation, inhibiting tribochemical reactions. However, when hydrogen is diluted with nitrogen, PTFE's tribological performance improves, though tribochemistry is not promoted. Only with oxygen and water vapour do tribochemical reactions occur in H₂, where metal fluoride is first formed, followed by carboxylate chelates. These findings highlight the critical role of hydrogen's reducing nature, offering insights for developing advanced sealing materials.

1. Introduction

In recent decades, hydrogen (H₂) has emerged as one of the most promising energy carriers to replace fossil fuels [1]. H₂ removes carbon emissions at the point of use [2,3], and has favourable combustion properties [4,5]. In aerospace applications, its low molecular weight is also an advantage [6]. H₂ is well established as fuel for fuel cells and its use in gas turbines and internal combustion engines is being actively researched.

The safe storage and transportation of H₂ gas are critical for its widespread adoption as an energy source. In compressed storage systems, internal pressures within compressors can reach up to 100 MPa [7]. To prevent contamination of H₂ by volatile substances such as lubricating oils and greases, oil-free reciprocating compressors are extensively employed [8], with sealing and lubrication dependent on the properties of sealing rings [9]. These components must meet rigorous standards, displaying low friction coefficients (COF) and wear rates against steel, to ensure optimal performance. These demanding specifications are pivotal to maintaining the purity of H₂ throughout its compression and subsequent transport phases.

The movement of sealing elements in high-pressure H₂ storage systems results in fretting, making the sealing more prone to failure compared to traditional sliding mechanisms [10–12]. Fretting refers to the wear that occurs on loaded contacting surfaces due to small oscillatory tangential movements, typically with sliding amplitudes ranging from micrometres to millimetres [13]. The debris generated from

fretting tends to be trapped in the contact between seal elements and metal surfaces [14]. It induces stress concentrations within the seal elements, leading to crack formation [11,12]. Fretting contributes to seal failure and subsequent H₂ leakage. Therefore, it is necessary to examine fretting failure when researching compressor sealing rings.

Generally, the production and transportation of H₂ may introduce contaminants. Common H₂ production methods such as natural gas reforming and electrolysis of seawater inevitably result in H₂O incorporation [15]. Furthermore, during transportation, the use of liquid ammonia (NH₃) as an H₂ carrier also leads to condensation, potentially increasing the H₂O content [15,16]. Therefore, in this work, we examine the impact of H₂O contaminants on the tribological properties of sealing elements in the H₂ environment by exploring the friction mechanisms under varying humidity conditions.

Polytetrafluoroethylene (PTFE) and its composites have demonstrated good self-lubricating properties with low COF and wear rates against metal surfaces [8,9]. Their compliance, elasticity, and excellent sealing properties make them preferred materials for seals in oil-free reciprocating compressors [9,17]. Additionally, PTFE composites exhibit outstanding chemical resistance [18] and lower H₂ permeability compared to metallic counterparts [19], making them suitable for H₂ sealing applications. For instance, Nakashima *et al.* and Sawae *et al.* found that PTFE exhibited lower wear in H₂ environments compared to air [20,21]. Their morphology and surface chemistry of wear tracks suggested that in H₂ the PTFE transfer films seem more complete than that in dry air, thus resulting in lower wear. However, Sakano *et al.* then

^{*} Corresponding author.

E-mail address: j.wong@imperial.ac.uk (J.S.S. Wong).

<https://doi.org/10.1016/j.triboint.2024.110481>

Received 24 October 2024; Received in revised form 9 December 2024; Accepted 21 December 2024

Available online 24 December 2024

0301-679X/© 2024 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

published a work with the opposite result, indicating that the wear of pure PTFE in H₂ was significantly higher than in air [22]. This high wear is caused by the continuously increased counterface roughness, indicating that a protective transfer film cannot form in H₂. These contradictory findings highlight the need for further investigation into PTFE tribological properties in H₂ environments.

In addition to neat PTFE, the impact of fillers, such as glass fibres (GFs), carbon fibres (CFs), polyphenylene sulfide (PPS), and graphite, on the tribological performance of PTFE composites in H₂ environments [8, 23, 24] have been investigated. It was found that soft fillers like PPS and graphite improved PTFE's wear resistance in H₂ by promoting the formation of transfer films, resulting in lower wear than in air [8]. Conversely, hard abrasive fillers such as GFs increased wear due to surface damage. However, in the case of another hard abrasive filler CFs, protective carbon-rich friction films were formed, which effectively reduced wear [8, 24]. Moreover, Nakashima *et al.* analyzed the effects of water contamination in H₂ applications [25]. They observed that increased humidity in H₂ enhanced the formation of transfer films on unfilled PTFE, thereby reducing wear. This was attributed to the promotion of iron hydroxide formation in humid environments, which facilitated the transfer film formation [25]. Chen *et al.* further explored the influence of water contamination on PTFE composites filled with CFs [26]. They found that carbon-based transfer films formed at very low (less than 1 ppm) and relatively high (more than 20 ppm) water contents, thus reducing wear. However, within the intermediate humidity range, the composites exhibited higher wear and friction coefficients.

The production of PTFE based materials has been significantly impacted by European regulations introduced in February 2023, restricting the use of PFAS materials, thus leading to a substantial reduction in PTFE production [27]. Identifying appropriate alternatives has become a matter of urgency. A thorough understanding of the friction reduction mechanisms of neat PTFE in H₂ environment can provide invaluable guidance for designing the next generation of sealing materials. However, studies on the lubrication mechanisms of neat PTFE in H₂ are scarce, and the existing experimental results are contradictory. Furthermore, few studies were conducted under fretting conditions, making it difficult to reference them for real-world compressor sealing scenarios. This study aims to fill these gaps. In this work, we focus on fretting and investigate the tribological performance and the formation of transfer films of neat PTFE in H₂ under varying humidity and O₂ levels.

2. Material and methods

2.1. Materials

Neat PTFE balls (PCS instruments) with a diameter of 6 mm were the model seal materials. 52100 steel discs with a diameter of 10 mm and a thickness of 3 mm (PCS instruments) and iron oxide discs of the same size were selected as counterfaces. The mechanical properties of test materials are listed in Table 1. The roughness of specimens was measured using a Confocal Microscope with a 20 × objective lens.

All PTFE balls were subjected to ultrasonic cleaning in isopropanol (99.9%, VWR CHEMICALS) for 10 minutes, then rinsed with isopropanol and dried with compressed air. Both 52100 steel and iron oxide discs underwent a 15-minute ultrasonic cleaning in heptane (99%, Fisher Chemical), followed by sequential washing with heptane,

acetone (pharmaceutical primary standard, VWR CHEMICALS), and isopropanol. They were then dried using compressed air.

2.2. Fretting test

Tribological experiments were conducted using a High Pressure Reciprocating Rig (HPR, PCS Instruments), see schematic Fig. 1. The HPR creates a point contact with a reciprocating ball (No. 10) pressed against a stationary disc (No. 11) in an atmosphere-controlled chamber. Note that the capacity of the HPR chamber is 20 mL. Control over gas flow entering the chamber was facilitated by an electronic flowmeter (No. 01), allowing accurate mixing of different gases. Specific mixing parameters are shown in STable 2 (Tables and figures starting with 'S' can be found in [supplementary information](#)). H₂ (99.99%) gas was from BOC. O₂ was introduced into the test via the use of dry compressed air (21% +/- 0.5% O₂ in N₂, from BOC) for safety reasons. N₂ cylinders (99.998%) were from BOC.

Humidity control within the chamber was done using a home-built water bottle system (No. 06, Fig. 1). By regulating the flow of gas, precise humidity levels were achieved (humidity ≈ RH 85%, as shown in SFig. 2). A hygrometer (No. 16) located at the chamber's outlet allowed for real-time monitoring of the experimental humidity. An O₂ sensor was attached to the outlet to measure the O₂ content in the chamber (No. 17, Fig. 1). For safety considerations, all experimental equipment was housed in a fume cupboard (No. 05, Fig. 1) to mitigate risks associated with H₂ leakage.

All experiments were conducted at a temperature of 60 °C, with a total gas flow rate of 0.3 L/min. Experimental conditions are detailed in Table 2. Tests labelled with 'D-' and 'W-' were tests conducted in dry gases and in 85% RH respectively. Most tests were conducted with a stroke length of 0.8 mm and a frequency of 31 Hz, achieving an average speed of approximately 0.05 m/s. The test duration was one hour, giving a total sliding distance of 178 m. Some tests (see test labels with 'F') were conducted with a stroke length of 1 mm and a frequency of 50 Hz, with a test duration set at 29 minutes. This gave an average speed of

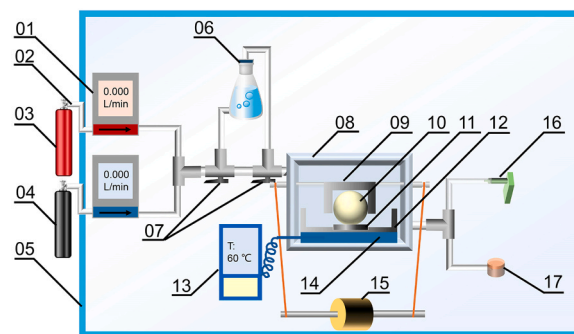


Fig. 1. Schematic diagram of experimental setup including 01: Flowmeter (Alicat Scientific company), 02: steel gas pipe (Swagelok company), 03: H₂ cylinder (BOC gas company), 04: other gas cylinders (N₂, Air, BOC gas company), 05: fume cupboard, 06: home-built liquid bottle (H₂O), 07: Three-way valve (Swagelok company), 08: HPR chamber, 09: HPR upper holder, 10: PTFE ball, 11: 52100 steel disc/iron oxide disc, 12: HPR lower holder, 13: PID temperature controller, 14: HPR heater, 15: weight, (08–15 constitute the HPR from PCS instrument company), 16: Hygrometer 17: O₂ sensor (FDO2, Pyrosience sensor technology company).

Table 1
The mechanical properties of materials.

Name	Hardness (Hv)	Young's modulus (GPa)	Poisson's ratio	Roughness (Ra/μm)
PTFE	2.65	0.60	0.46	1.735
52100 steel discs	200	210	0.29	0.02
Iron Oxides	680	200	0.25	0.31

Table 2

Experimental conditions and test naming in this work. Pressure is calculated with PTFE ball vs. steel disc.

Test name	Load (N) / Initial Hertzian average pressure (MPa)	Average Sliding Speed (m/s)	Atmosphere	O ₂ Percentage (%) VOL)	Humidity
D-2 N	2 / 19.43	0.05	H ₂	0	Dry
W-2 N	2 / 19.43	0.05	H ₂ / H ₂ O vapour	0	RH 85 %
Dry	4 / 24.48	0.05	H ₂	0	Dry
Wet	4 / 24.48	0.05	H ₂ / H ₂ O vapour	0	RH 85 %
D-2 N-F	2 / 19.43	0.10	H ₂	0	Dry
W-2 N-F	2 / 19.43	0.10	H ₂ / H ₂ O vapour	0	RH 85 %
D-F	4 / 24.48	0.10	H ₂	0	Dry
W-F	4 / 24.48	0.10	H ₂ / H ₂ O vapour	0	RH 85 %
D-2 % O ₂	4 / 24.48	0.05	90 % H ₂ & 2 % O ₂ & 8 % N ₂	2	RH 85 %
W-2 % O ₂	4 / 24.48	0.05	90 % H ₂ & 2 % O ₂ & 8 % N ₂ / H ₂ O vapour	2	RH 85 %
D-5 % O ₂	4 / 24.48	0.05	75 % H ₂ & 5 % O ₂ & 20 % N ₂	5	RH 85 %
W-5 % O ₂	4 / 24.48	0.05	75 % H ₂ & 5 % O ₂ & 20 % N ₂ / H ₂ O vapour	5	RH 85 %
D-10 % O ₂	4 / 24.48	0.05	50 % H ₂ & 10 % O ₂ & 40 % N ₂	10	RH 85 %
W-10 % O ₂	4 / 24.48	0.05	50 % H ₂ & 10 % O ₂ & 40 % N ₂ / H ₂ O vapour	10	RH 85 %
D-Air	4 / 24.48	0.05	21 % O ₂ & 78 % N ₂	21	RH 85 %
W-Air	4 / 24.48	0.05	21 % O ₂ & 78 % N ₂ / H ₂ O vapour	21	RH 85 %
W-Iron	4 / 24.48	0.05	H ₂ / H ₂ O vapour	0	RH 85 %
Oxide					
D-10 % N ₂	4 / 24.48	0.05	90 % H ₂ & 10 % N ₂	0	Dry
W-10 % N ₂	4 / 24.48	0.05	90 % H ₂ & 10 % N ₂ / H ₂ O vapour	0	RH 85 %
D-20 % N ₂	4 / 24.48	0.05	75 % H ₂ & 25 % N ₂	0	Dry
W-20 % N ₂	4 / 24.48	0.05	75 % H ₂ & 25 % N ₂ / H ₂ O vapour	0	RH 85 %
D-50 % N ₂	4 / 24.48	0.05	50 % H ₂ & 50 % N ₂	0	Dry
W-50 % N ₂	4 / 24.48	0.05	50 % H ₂ & 50 % N ₂ / H ₂ O vapour	0	RH 85 %
D-N ₂	4 / 24.48	0.05	N ₂	0	Dry
W-N ₂	4 / 24.48	0.05	N ₂ / H ₂ O vapour	0	RH 85 %

approximately 0.1 m/s and a total sliding distance of 174 m. According to the calculations shown in **STable 1 (in S02)**, when the load was 4 N, the initial Hertzian contact diameter was about 0.46 mm. Due to wear, the final contact diameter was about 1.60 mm (**STable 1**). Note that the stroke length of the test was comparable to the Hertzian contact width. Hence, the movement is in a fretting-like motion [28].

To investigate the evolution of worn surfaces during rubbing, some tests were intermittently stopped to examine these surfaces ex-situ before continuing the tests. COFs and the worn surfaces at the end of tests with and without intermittent stops were similar, suggesting such a process did not affect our results (see **SFig. 14**).

2.3. Surface analysis

Rubbed surfaces of balls and discs were observed using an optical microscope (RH-2000 system, MXB-2500REZ Lenses, HiRox Europe). White Light Interferometry (Bruker GT-K) was used to examine the transfer film morphology. The microscope has a 5× objective lens. LEXT® OLS5000 3D Laser Confocal Microscope, equipped with a 405 nm laser, and a 10×, a 20× and a 100× objectives were used to observe the morphology of the worn PTFE ball surface. A circular region with a diameter of 500 µm at the centre of the view field was selected, and the R_a value of the measured area was taken as the roughness of the specimens.

Fourier Transform Infrared Spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS), and Raman spectroscopy were used to analyze the chemical composition of rubbed metal disc surfaces. FTIR analysis was conducted using a MultiScope FT-IR system (PerkinElmer), operating in reflectance mode. This system is equipped with a built-in tungsten/halogen illuminator with a variable power of up to 35 W. It utilizes a medium-band MCT detector with a signal-to-noise ratio, typically better than 9000/1 peak-to-peak and 45,000/1 rms. The measurements were taken through a 100 µm diameter aperture with a resolution of 4 cm⁻¹ over a spectral range of 200–2000 cm⁻¹. Each spectrum was collected over 20 scans.

X-ray photoelectron spectroscopy (XPS) analysis was performed using a Thermo NEXSA instrument. This system is equipped with a Mono

Al K-alpha X-ray source, which operates at an energy of 1486.69 eV and a strength of 72 W. The spot size was set to 200 × 100 µm². Charge compensation was achieved using Thermo Scientific's dual-beam low-energy electron/ion source (FG-03), with the ion gun operating at a current of 150 µA and a voltage of 45 V. Measurements were conducted under ultra-high vacuum conditions with a pressure below 10⁻⁸ PSI. The temperature during the analysis was maintained at 294 K. The survey spectra pass energy was set at 150 eV, while the region-specific spectra utilized pass energy of 40 eV. XPS high resolution spectra were calibrated by using C 1 s as a reference at 284.8 eV.

Raman spectroscopy was performed using a Raman alpha300 system (WITec focus innovations company). The microscope has a 20 × objective lens and spectra were taken with an integration time of 0.5 s for 100 accumulations. The laser used has a wavelength of 532 ± 15 nm. The laser power was ca 3 mW, and the beam size was 2.4 µm.

3. Results

3.1. Effect of H₂O in pure H₂

The effects of load and speed on friction coefficient (COF) of PTFE-steel contacts in dry and wet H₂ are shown in **Fig. 2**. Each test was performed at least twice with good reproducibility, although results from high speeds are slightly more varied. Note that the effects of applied load and speed on COF are weak.

Although the applied load and sliding speed do not affect the COFs, they influence the wear of PTFE. **Fig. 3(a)** shows the wear volume calculated by measuring the size of the wear scar on the PTFE ball (see calculations in **S3-1** and **S3-2** and diagram **SFig. 3 of S03**). As expected, wear volume increases with the load. The final average contact pressure is calculated based on the area of wear scar on the ball at the end of the tests, and it increases with applied load, see **Fig. 3(b)** and (c). Notably, this is much lower than the compressive yield strength of PTFE (approximately 15 MPa) [29]. The inclusion of H₂O in H₂ reduces the wear volume slightly, see **Fig. 3(a)**. The morphology of the transfer film on steel formed in dry H₂ (test *Dry*) is heterogeneous and discontinuous, consisting of ribbon-like streaks and layers (see **SFig. 4**). Its thickness

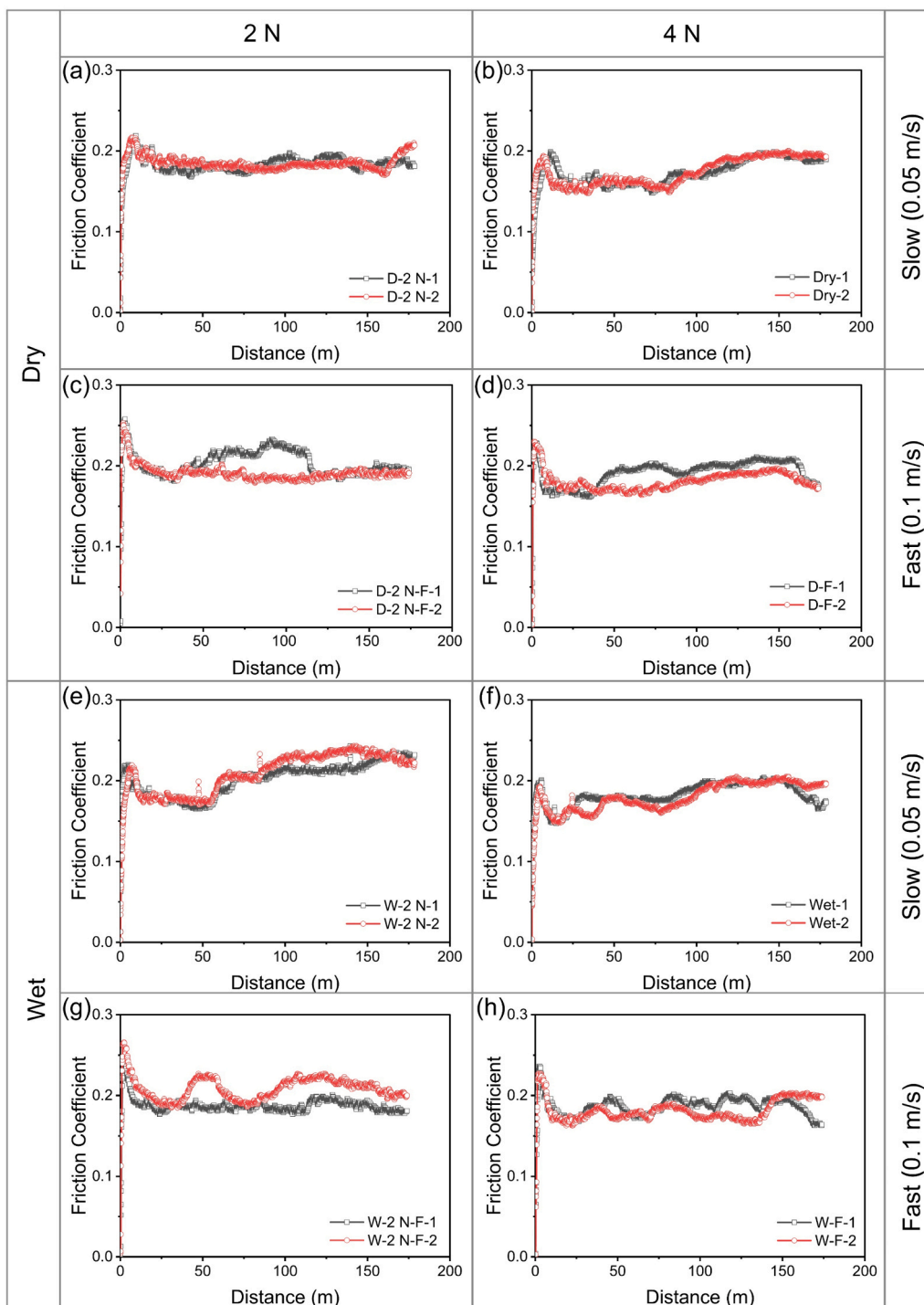


Fig. 2. COF results obtained in dry H_2 (*Dry*) and humid H_2 (*Wet*) with a relative humidity of RH 85 %, loads of 2 N and 4 N and average sliding speeds of 0.05 m/s (*Slow*) and 0.1 m/s (*Fast*).

ranges from 0 μm to 35 μm . With increased humidity (test *Wet*), the morphology of the transfer film is similar to that in the dry condition, with thickness ranging from 0 μm to 21 μm (see **SFig. 5**).

When speed increases from 0.05 m/s to 0.1 m/s, a slight increase in wear volume is observed noticeably at high load (see **Fig. 3(a)**). Recall the rubbing distance was fixed. At a higher speed, frictional heating may affect the properties of the polymers, leading to more wear. Note that the estimated maximum flash temperature occurs at the initial state under 4 N and 0.1 m/s, is only 2.03 K (see calculation in **S04**), which is modest compared to the experimental temperature of 60 $^{\circ}\text{C}$. Additional analysis

has been conducted using the thermos-mechanical model developed in [30] to take into account of the roughness of surface surfaces. Note the applied model was for a line contact and so the estimate was done using an average pressure similar to that used in our tests (which were point contacts). The surface topography of the PTFE ball was one of the input of the model. The maximum temperature at asperities was < 3 K which is closed to the estimated flash temperature of the contact. This is probably due to the low strength of PTFE, and hence its asperities were ironed out quickly. This supports that frictional heating in our experiments can be considered negligible, and unlikely to affect our results.

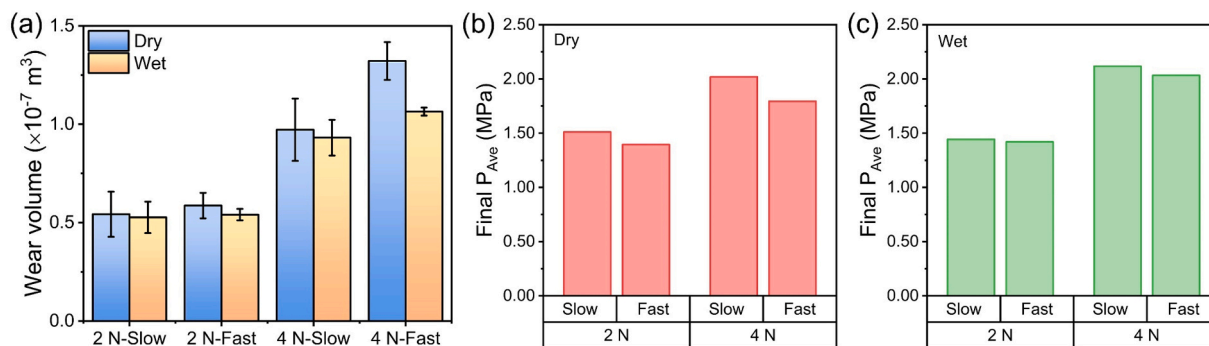


Fig. 3. (a) Comparison of PTFE wear volume in H_2 under different experimental conditions (each test repeated at least 2 times), and the corresponding specific wear rates are shown in **SFig. 15**. Average values of contact pressure in (b) dry and (c) wet conditions at the end of the friction experiments (details shown in **STable 3**).

As COF is insensitive to load and speed, while wear increases with load and speed as expected, only results from low speed and high load conditions, specifically 0.05 m/s and 4 N, are mainly used for the subsequent discussions.

3.2. Effect of N_2 and O_2 in H_2

The effect of O_2 in H_2 was investigated in this work by the introduction of dry air. Since the major component of air is N_2 , the effect of N_2 on the tribology of PTFE-steel contact in H_2 was first examined. The steady state COF in various concentrations of N_2 in H_2 is in **Fig. 4**. In a dry H_2 environment, introducing N_2 decreases steady state COF (black in **Fig. 4(a)**) and PTFE wear (see **Fig. 5(a)**), with the most significant drop occurs at 10 % N_2 .

The reduction in COF in H_2 by N_2 dilution is less when O_2 (in the form of air, see **Fig. 4(b)**) or water (in the form of humid H_2 , see **Fig. 4(a)**) is introduced into the gas mixtures, as such the steady-state COF becomes relatively insensitive to composition of the mixture. This shows that a small amount of O_2 and water governs the properties of the PTFE-steel contact in H_2 -air mixture.

In dry H_2 , the reduction in PTFE wear by dilution is insensitive to the composition of the gas mixture. In wet H_2 more substantial PTFE wear reduction is observed only if the gas mixture has 10 % or more O_2 . N_2 dilution in wet and dry H_2 gives similar amount of PTFE wear. While diluting wet H_2 with air gives a similar COF to that in dry H_2 (**Fig. 4(b)**), PTFE wear is lowered in the former (**Fig. 5**). Previous literature indicated that both O_2 and H_2O are essential for producing uniform, stable, and wear-resistant PTFE tribofilms [31,32]. It may explain the reduced wear with the inclusion of O_2 in wet H_2 . Together with the friction results, however, this tribofilm may not give substantial friction reduction.

Worn surfaces of PTFE were observed using a confocal microscope with 10 $\times$ and 100 $\times$ objectives. The unworn surface (shown in **SFig. 23**) appears lumpy. After rubbing, the worn surfaces look streaky,

as shown in **SFig. 17** to **SFig. 22**. Similar worn PTFE ball surfaces were observed regardless of test environment (H_2 , air, or O_2 -mixed H_2) or humidity. Distinct grooves on these surfaces may be due to abrasive wear [33] from metal or oxide debris. Plastic deformations, such as ironing of asperities and stretching of PTFE debris, may also contribute to the observed worn surfaces.

3.3. Effect of O_2 on tribofilm formation in wet H_2

Section 3.2 shows that the amount of PTFE wear in PTFE-steel contacts is reduced in humid H_2 only when 10 % O_2 or more (in the form of air) is introduced. In addition, a small amount of O_2 is sufficient to remove the benefit N_2 dilution brings to PTFE friction reduction in dry H_2 . Clearly, oxygen plays a determining role in the air/ H_2 ambient. In this section, the evolution of the transfer film in humid H_2 (Wet) and humid air (W-Air) is compared.

All friction curves (see **Fig. 6**) show the following features; COF increases initially. It reaches a maximum, it drops and then stabilises at a low value. In some cases, it rises slightly before it stabilises. The part of the friction curve before COF stabilises is commonly attributed to the running in process, which may be related to transfer film formation. Steel wear tracks were observed intermittently during friction tests. Micrographs of wear tracks formed in wet H_2 (**Fig. 6(a)**, Wet) show lumps of polymer after 2 min of rubbing. These lumps form aggregates, which cover part of the track. At the steady state, some ribbon-like films can be seen under the aggregates. Conversely, in wet air (**Fig. 6(b)**, W-Air), the COF rises more slowly to the maximum before a relatively gentle decline. Micrographs of its steel wear scar shows no significant lump formation during the running-in process after 5 min of rubbing. Ribbon-like films are observed at a steady state. They seem thinner than those formed in wet H_2 . The amount of PTFE wear, even during running-in (**SFig. 13**), is lower in wet air than in wet hydrogen. This suggests that the difference in transfer film formation process may explain reduced

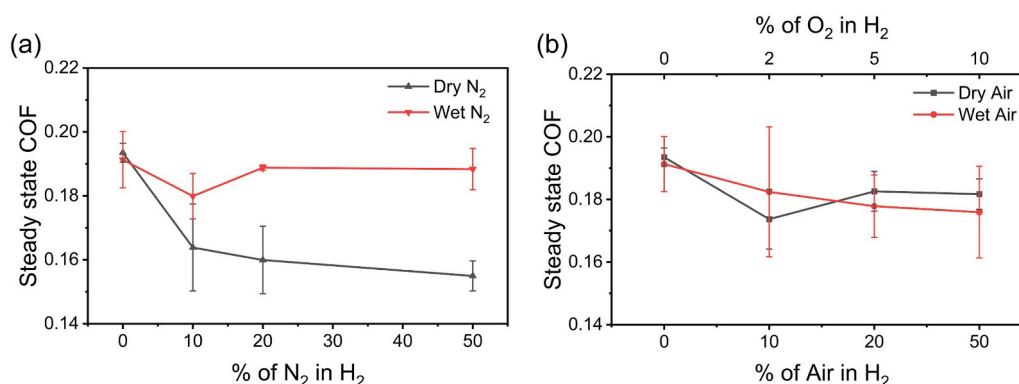


Fig. 4. The average COF value of the last 30 m in friction tests. COF curves are shown in **SFig. 11** and **SFig. 12**.

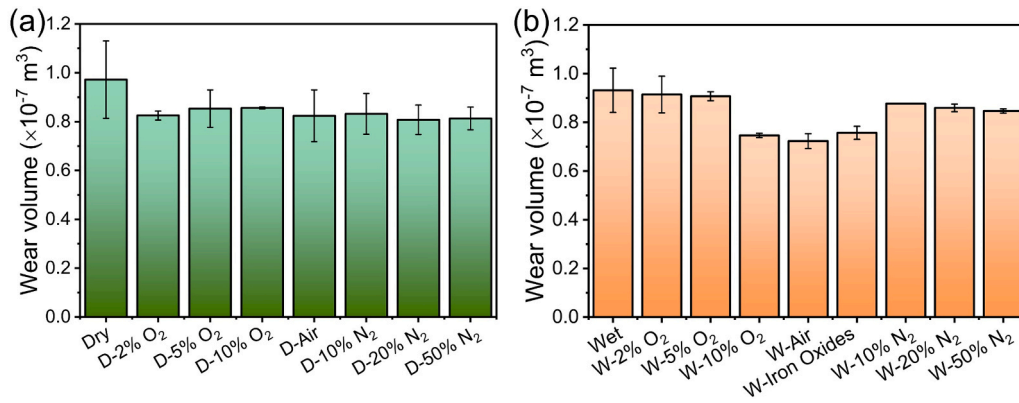


Fig. 5. (a) The wear volume of tests in dry conditions: Dry, D-2 % O_2 , D-5 % O_2 , D-Air, D-10 % N_2 , D-20 % N_2 , and D-50 % N_2 . (b) The wear volume of tests in humid conditions: Wet, W-2 % O_2 , W-5 % O_2 , W-Air, W-Iron Oxides, W-10 % N_2 , W-20 % N_2 , and W-50 % N_2 . Test conditions: applied load = 4 N, average sliding speed = 0.05 m/s (each test repeated at least 2 times). The corresponding specific wear rates are shown in SFig. 16.

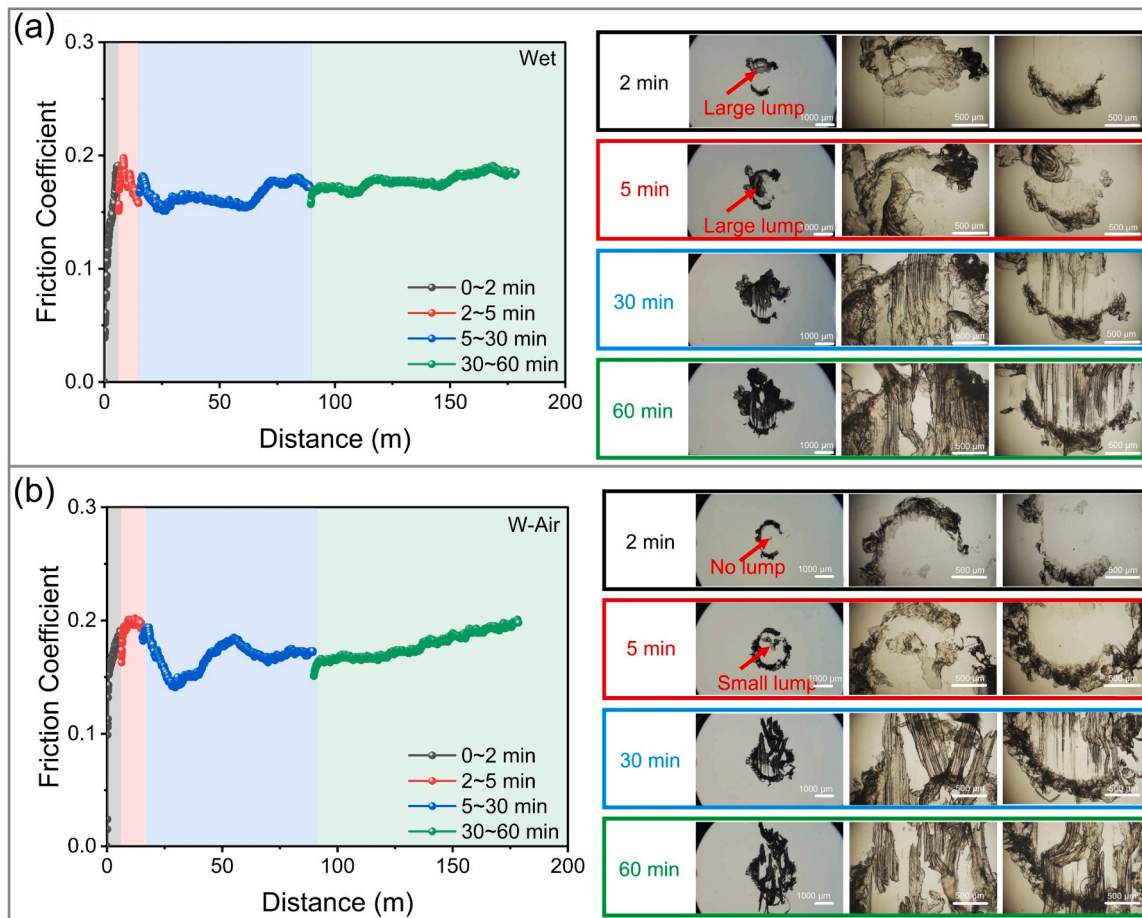


Fig. 6. The COF results and the morphology of the transfer film on the steel counterface after rubbing for 2, 5, 30, and 60 mins of (a) Wet hydrogen and (b) Wet Air. Tests were conducted under the conditions of 4 N and 0.05 m/s.

PTFE wear in the presence of O_2 in humid H_2 .

Friction curves obtained in humid H_2 (85 % RH) with 0, 2, 5 % and 10 % O_2 (i.e. 0, 10, 20 and 50 % air in wet H_2) and that in wet air are presented in Fig. 7(a). The running-in distance is defined as the rubbing distance covered to reach the steady state COF, see arrows in Fig. 7(b) (see also SFig. 8). It increases with increasing O_2 content in the test ambient (see Fig. 7(c)). Note that, as shown in Fig. 5(b), PTFE wear volume reduces as O_2 content increases. Interestingly the relationship between running-in distance and % O_2 is not seen in dry H_2 , nor when N_2

is the sole dilutant. Based on the results in Fig. 6, it is possible that increasing O_2 content results in less lumpy transfer films being produced and hence reduces PTFE wear. This may affect the time it takes for COF to stabilise.

4. Discussions

Our results show that the tribological performance of PTFE-steel contact under fretting conditions strongly depends on the gaseous

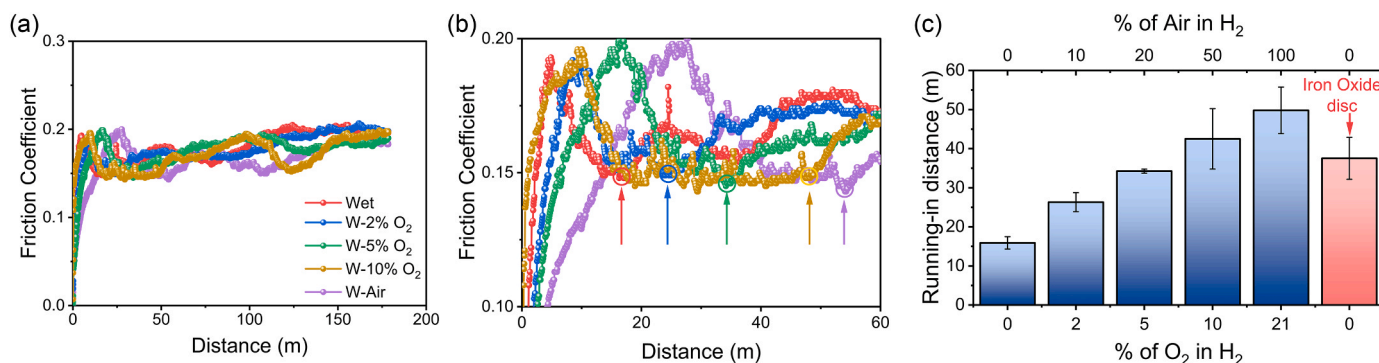


Fig. 7. (a) The results of the COF curve from the experiments *Wet* (0 % O₂), *W-2 % O₂*, *W-5 % O₂*, *W-10 % O₂*, and *W-Air* (21 % O₂); (b) COF focusing on the first 60 m of (a), arrows indicate the running-in distance; (c) the distance of the running-in process. Test conditions: applied load = 4 N, average sliding speed = 0.05 m/s.

environment. Comparing the performance in pure dry H₂ and pure dry N₂, only dry N₂ gives both low friction and low wear. This is different from what was observed in steel-steel contacts where pure H₂ and pure N₂ give similarly high friction, indicative of adhesive wear [34]. Note that H₂ reduces iron oxide but N₂ does not. Thus the difference here may stem from how PTFE reacts with iron oxide. Our results also show that the existence of O₂ and water impacts PTFE tribology in H₂ significantly. The effect of O₂ and water may again stem from its influence of surface oxide chemistry which has also been shown to affect friction and wear in steel-steel contact [35].

In many studies on PTFE tribology, the friction and wear of PTFE are governed by the formation of polymeric transfer layers on the counterface. Transfer films in this study are defined as polymeric materials adhered to steel surfaces during rubbing tests. In this study, these transfer films are categorized based on the absence or presence of tribochemical reactions during film formation. The former is an adhered film, while the latter is a tribofilm which usually contains Metal-F bonds or metal carboxylate chelates. It has been proposed that the formation of tribofilms, which is promoted by humidity [25], can significantly reduce wear [36–38]. While these studies were mostly conducted in humid air (the main components are O₂ and N₂), these mechanisms may apply to humid H₂. Surface chemical analysis were carried out to examine how O₂ and water affect steel surface chemistry of wear scars formed in H₂.

4.1. Polymer transfer films formed in H₂

This section focuses on the chemistry of transfer films formed in H₂. The FTIR spectrum of bulk PTFE (see in SFig. 6) contains peaks at 1149 cm⁻¹ and 1205 cm⁻¹ which are assigned to the asymmetric and symmetric stretching vibrations of the CF₂ [38,39]. These peaks are observed in the FTIR spectra of transfer films (Fig. 8) formed in both wet

and dry H₂. This confirms that the main component of these transfer films is bulk PTFE. Some of the PTFE chains of these transfer films are conformationally distorted, as suggested by the peak at 1254 cm⁻¹ [32, 39]. Since these spectra have no peaks at 1449 cm⁻¹ and 1650 cm⁻¹, there is no evidence of metal carboxylic chelates forming in an H₂ environment regardless of humidity (see Fig. 8) [38,40,41].

XPS spectra of transfer films formed in dry and wet H₂ atmosphere (test *Dry* and *Wet*) are presented in Fig. 9. The C 1 s spectra (shown in Fig. 9(a) and STable 5) and the O 1 s spectra (shown in Fig. 9(c) and STable 7) contain peaks from C-O (286.00 eV in C 1 s, 531.61 eV in O 1 s) and C=O (288.50 eV in C 1 s, 532.80 eV in O 1 s) moieties [26,42]. Since there are no peaks for carboxylic groups on the FTIR spectrum (Fig. 8) and no peak on XPS O 1 s in 535.65 eV [42,44], they are likely due to adventitious carbon [26]. Note these peaks are also found in the spectra of pristine metal discs in H₂ or air (as shown in SFig. 7, STable 5 and STable 7). Therefore, there is no evidence that a chelation reaction between carboxylates and metal has occurred in a dry (test *Dry*) or wet H₂ (test *Wet*) environment. No peak associated with Metal-F bonds, i.e. 685.00 eV [42,43] in the F 1 s spectrum (Fig. 9(b) and STable 6) and 714.5 eV [45] in the Fe 2p spectrum (Fig. 9(d) and STable 8), are found in both dry (test *Dry*) and wet H₂ (test *Wet*). This again supports that no tribochemical reaction has taken place during rubbing in H₂ and the main component of the transfer film is PTFE.

In wet H₂ (test *Wet*), the Fe 2p_{3/2} Fe(III) peak appears at 711.10 eV, which suggests the presence of iron hydroxide (Fe(III)-OOH) [46–48]. This is confirmed by the peak at 533.33 eV in the corresponding O 1 s spectrum, as shown in Fig. 9(c) and STable 7. For the transfer film formed in dry H₂ (test *Dry* in Fig. 9(d) and STable 8) however, the Fe

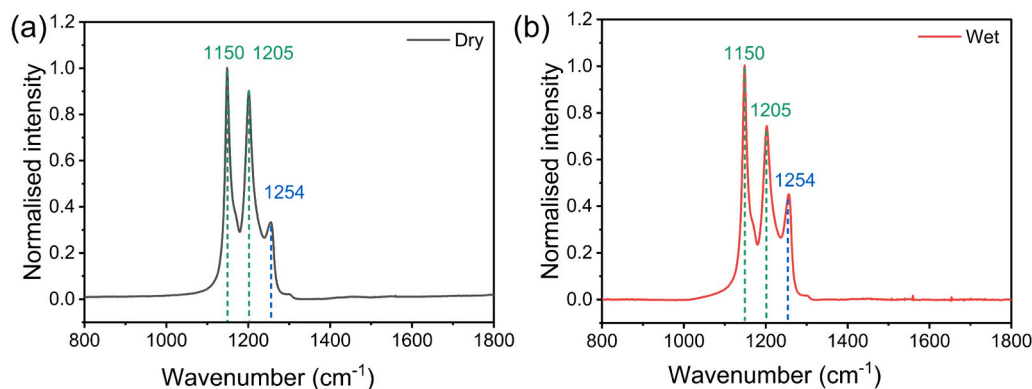


Fig. 8. The normalized FTIR spectra of the transfer films formed in H₂: test (a) *Dry*, and (b) *Wet*. Normalisation was done by setting the intensity of the peak at 1150 cm⁻¹ = 1.

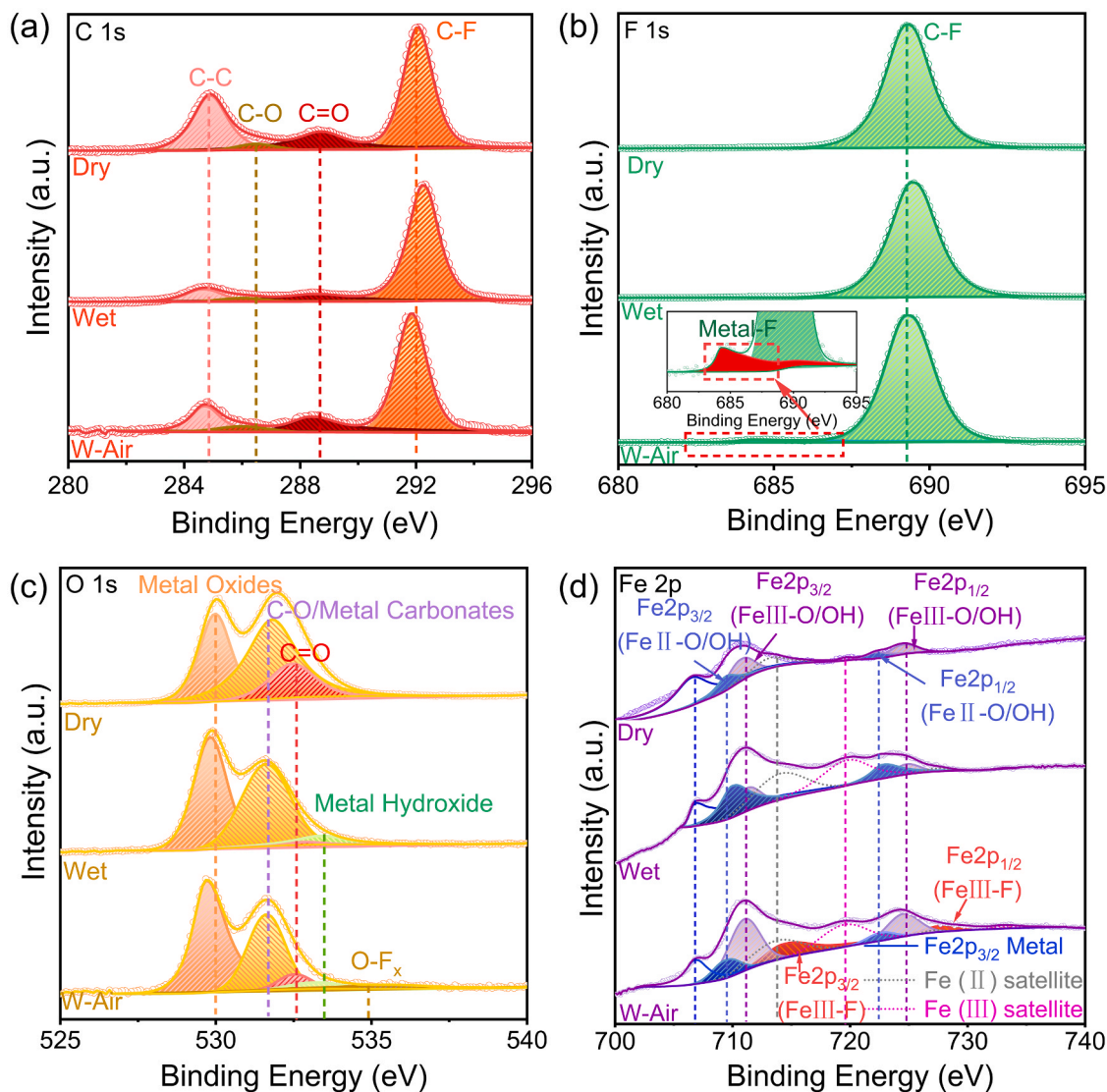


Fig. 9. The XPS results from test Dry, Wet, and W-Air, including the (a) C 1s, (b) F 1s, (c) O 1s, and (d) Fe 2p signal.

2p_{3/2} Fe(III) peak is at 710.66 eV, which can be assigned to iron oxides [49,50]. So, the presence of H₂O favours formation of iron hydroxide on rubbing metal surfaces. Despite the differences in surface oxides, similar transfer films formed in dry and wet H₂, giving similar tribological behaviour.

The tribochemical process of PTFE tribofilms formation on steel is believed to involve O₂ and H₂O reacting with PTFE molecular chains to form carboxylic groups, which then interact with metals to form metal chelates [32,40]. XPS O1s spectrum (Fig. 9(c), STable 7) of transfer film generated in wet air (test W-Air) has a peak at 535.65 eV which can be assigned to O-F bond [42,44]. This indicates the formation of carboxylic acid and metal chelates [40]. Its F1s spectrum (see Fig. 9(b)) shows a peak at 684.45 eV, indicating the formation of the Metal-F bond [51]. The peak of FeF₃ at 714.3 eV on its Fe 2p spectrum is also observed (see Fig. 9(d)) [45,49]. This confirms that in wet air, tribofilms containing iron fluoride is formed [40]. This is not seen in a pure H₂ environment. Our results suggest that the existence of water alone in H₂ is not sufficient to promote tribochemical reactions between transfer film and steel. This may explain the difference in film morphology and PTFE wear in wet H₂ and wet air (Fig. 6).

4.2. Polymer transfer films in a mixture of H₂ and air

FTIR spectra of steel wear scars formed in humid air/H₂ mixtures (see Fig. 10) show a peak at 1449 cm⁻¹. This is assigned to the chelation between degraded PTFE and the steel counterface [40]. Note that the intensity of the peak increases with increasing O₂ content. Therefore, in the wet H₂ atmosphere, tribochemical reactions can occur as long as some O₂ exists. This tribofilm may explain why PTFE wear reduces with O₂ content in H₂. The peak at 1550 cm⁻¹ in the FTIR spectrum can be assigned to C-O and C=O bonds [52].

4.3. How H₂ affects the formation of PTFE transfer films on steel

The differences in tribological performance of PTFE-steel contacts in air and in H₂ may stem from the strength of H₂ as a reductant. According to the details of the XPS O 1s spectra (STable 7), the atomic fraction of the metal oxide on worn surface formed in H₂ is always lower than that formed in air. For pristine disc, it is 18.0 % in dry H₂ vs. 27.1 % in dry air. For rubbed surfaces, it is 45.5 % in wet H₂ vs. 51.5 % in wet air. While Fe(II) is dominant in the iron oxide layer of rubbed surfaces in wet H₂ (Fe(II): Fe(III) = 64.3 %: 35.7 %), Fe(III) dominates in wet Air (Fe(II): Fe(III) = 43.7 %: 56.3 %, see STable 8). Hui et al. has shown that the formation energy of FeF₃ and FeF₂ are -938 kJ/mol and -642 kJ/

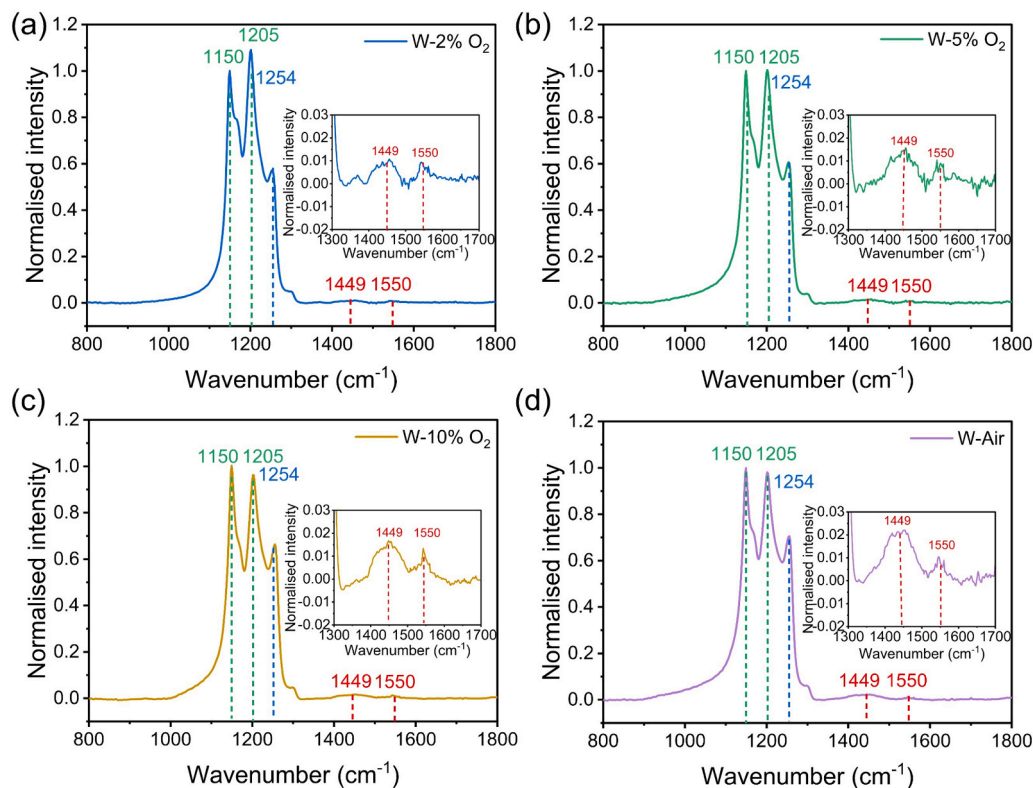


Fig. 10. FTIR spectra of wear scars (a) W-2 % O₂, (b) W-5 % O₂, (c) W-10 % O₂, and (d) W-Air tests. Spectra normalised by setting peak intensity at 1150 cm⁻¹ = 1. Insets are magnified views of spectra in the region between 1300 – 1700 cm⁻¹.

mol respectively [53], making the formation of FeF₂ less favourable. Hence our results support that H₂ inhibits tribological reaction by reducing the valence state of iron. The tribological results of PTFE against iron oxide discs, primarily composed of Fe₂O₃ (shown in SFig. 9), confirm this view, showing significantly reduced wear (Fig. 5 (b)) and increased run-in distance (Fig. 7(c)) in humid H₂.

Compared to Fe₂O₃, the reaction between Fe(OH)₃ and F yields an even more negative overall Gibbs free energy [54–56]. Therefore, the presence of H₂O and O₂ in a H₂-rich environment can lower the formation energy of Fe-F bonds, thereby promoting the tribochemical reaction, as hypothesized in Eqs. 3.1 to 3.3. First, iron in the steel disc reacts with environmental O₂ to form a layer of Fe₂O₃ on its surface. In a humid environment, H₂O reacts with this oxide layer to produce the relatively reactive Fe(OH)₃. Finally, Fe(OH)₃ reacts with individual F atoms or fluorine-containing dangling chains generated by mechanical shearing of PTFE during the friction process, resulting in the formation of Fe-F bonds. The reducing nature of H₂ inhibits the process shown in Eq. 3.1, preventing the formation of Fe₂O₃ and instead forming FeO. In a dry environment, the absence of H₂O prevents the reaction shown in Eq. 3.2 from occurring. Therefore, the presence of H₂ and the lack of H₂O suppresses the reaction of 3.1 and 3.2, thus increasing the energy barriers of the Metal-F bond formation.



From Eq. 3.1, the existence of O₂ is necessary for the promotion of PTFE tribofilm formation. Fig. 11 compares the XPS spectra of wear scars formed in wet air (W-Air-2 min) and wet H₂ (Wet-2 min) after 2 mins of rubbing. The XPS C 1s spectrum of Wet-2 min is dominated by the C-F peak, with an atomic ratio of 65.60 % (see in STable 5). In contrast, for W-Air-2 min, the atomic ratio of C-F is only 21.84 %. These

results align with the large lumps observed in Fig. 6. Even with only two minutes of rubbing, Wet-2 min has more Fe(II) (atomic ratios of Fe(II): Fe(III) = 61.7 %: 38.3 %), while for W-Air-2 min, Fe(III) dominates (Fe(II): Fe(III) = 39.9 %: 60.1 %, see STable 8). This confirms that the reduction of iron ions in H₂ occurs at early stage of rubbing. Most importantly, only for W-Air-2 min, peaks of Metal-F bond and FeF₃ compound peaks were identified at positions 684.90 eV [42,43] and 714.50 eV [45] in its F 1s and Fe 2p spectra respectively (Figs. 11(b) and 11(d), and STable 6 and STable 8), indicating the presence of tribochemical reactions during the running-in process. However, the O-F peak (at about 535.65 eV in the O 1s spectrum) was not observed in the O 1s spectrum [42,44], suggesting that chelates have not been formed at this stage. Therefore, we can conclude that the tribochemical reactions during the running-in process are dominated by the formation of the Metal-F bonds, while the steady-state rubbing sees the formation of chelates. The Metal-F bonds during running-in process improves interfacial adhesion between PTFE and steel. This is crucial for minimizing back transfer and debris formation and is necessary for tribofilm film formation and reducing wear [57,58]. This is evidenced by the smaller slope of wear volume change during the initial stage of the W-Air test, as shown in SFig. 13(a). The formation of metal carboxylates enhances the mechanical properties and exfoliation of PTFE, further promote the formation of a transfer film [59]. This makes the film more stable, thinner and uniform, resulting in improved wear suppression [59,60]. As shown in SFig. 13(a), the decrease of wear rate is evident i. No evidence of metal-F or Fe-F bonds is observed in XPS spectra in humid H₂, showing that water alone is not sufficient to promote PTFE tribofilm formation in H₂ gas.

4.4. How N₂ affects the transfer film formation

Based on the tribological results, H₂ diluted with N₂ can reduce the COF and wear under dry conditions, but this dilution effect disappears when water is present (Fig. 4 and Fig. 5). According to the FTIR results in Fig. 12(b) and (c), carboxylate chelates do not form in either dry or wet

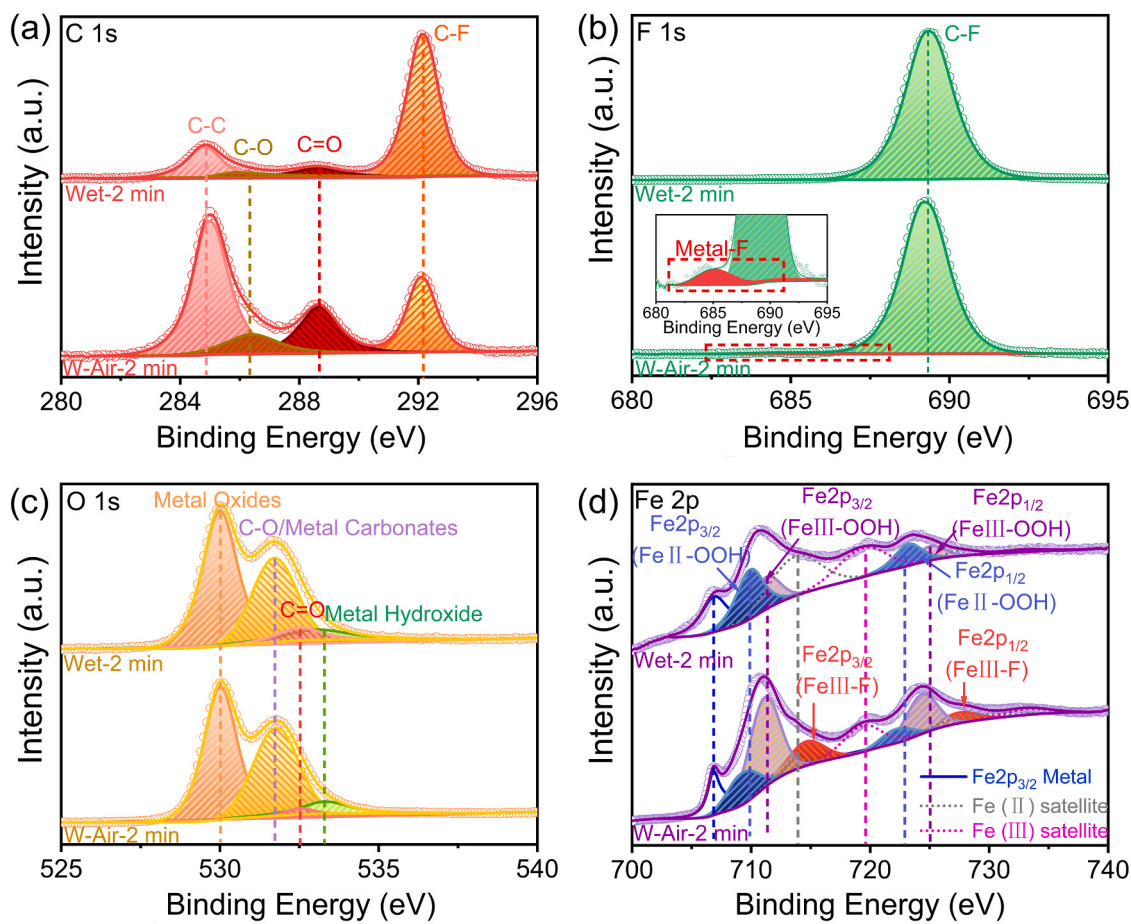


Fig. 11. The XPS results from the test Dry, Wet, and W-Air after 2 min rubbing process, including the (a) C 1 s, (b) F 1 s, (c) O 1 s, and (d) Fe 2 p signal.

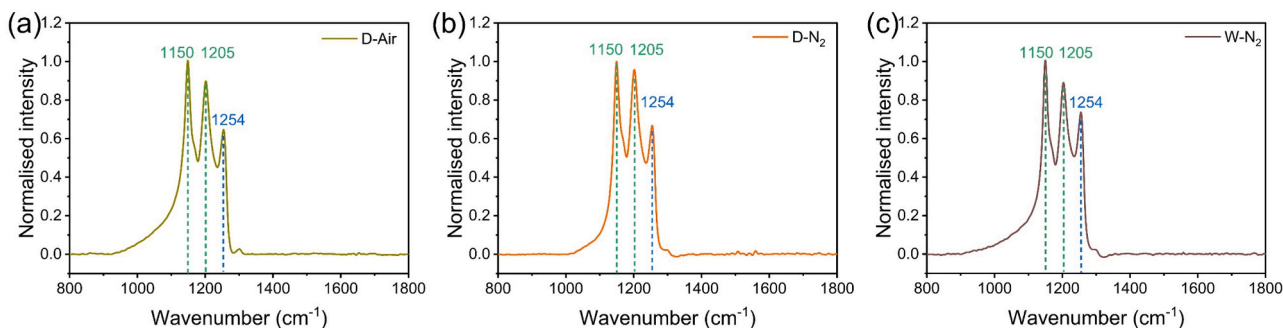


Fig. 12. The FTIR results of (a) D-Air, (b) D-N₂, and (c) W-N₂. Spectra normalized by setting peak intensity at 1150 cm⁻¹ = 1.

pure N₂ environments, as no relevant peaks can be observed at 1449 cm⁻¹ [38,40,41]. Therefore, the diluting effect of N₂ in dry H₂ may simply be due to decreasing H₂ concentration, thereby weakening the reducing ability of the ambient. Additionally, unlike wet air (Fig. 10(d)), as shown in Fig. 12(a), no tribochemical reactions occur in dry air (O₂, 21 %), indicating that water is necessary for the formation of carboxylate chelates. Therefore, N₂ does not participate in the tribochemical reaction; the factors influencing tribochemical reactions are water and O₂.

5. Conclusion

This study investigated the tribological performance and tribochemical mechanisms of neat PTFE in fretting conditions, under varying humidity levels and O₂ concentrations in H₂-rich environments.

It aimed to elucidate the tribological behavior of pure PTFE-steel contacts in these conditions, thereby providing guidance for the design of a new generation of self-lubricating polymers.

Our findings reveal that: (1) H₂ ambient contributes to increased PTFE wear in PTFE-steel contacts; (2) no tribochemical reaction between PTFE and steel occurs in pure H₂ regardless of humidity levels; (3) XPS and FTIR results support that tribochemical reactions between PTFE and steel occur in H₂ gas in the presence of moisture and O₂; (4) the strong reducing nature of H₂ reduces the amount of surface metal oxides and converts trivalent iron (Fe(III)) to divalent iron (Fe(II)), inhibiting the formation of Fe-F bonds thus preventing tribochemical reactions; (5) a reactive Fe(OH)₃ layer forms on steel surfaces in the presence of H₂O and O₂, promoting Fe-F bond formation; (6) Metal-F bonds form at the initial stage of rubbing, while metal carboxylate chelates develop later, playing a key role in wear reduction.

Our study contributes to a deeper understanding of tribological performance of PTFE-steel contacts under fretting conditions in H₂ environments, which is relevant to applications such as PTFE compressor seal rings. Additionally, by studying behaviour of pure PTFE, we gained insights into the requirements of the next generation of self-lubricating polymer alternatives for H₂ applications. Such materials should be exfoliative, forming a protective polymer film on the counter surface, and should contain elements that easily bond with metal ions to promote tribochemical reactions and reduce wear.

In conclusion, this research enhances our understanding of the tribology of PTFE in H₂ environments through detailed chemical characterization and informs the development of alternate polymers suitable for H₂ compressor applications.

CRediT authorship contribution statement

Shouyi Yin: Writing – original draft, Investigation, Formal analysis. **Ambrose Taylor:** Supervision. **Janet S. S. Wong:** Writing – review & editing, Supervision, Project administration, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

S.Y. is grateful for the financial support by Department of Mechanical Engineering, Imperial College London. The authors would like to thank Dr Jie Zhang for technical support. X-ray photoelectron (XPS) data was acquired at the EPSRC National Facility for XPS (“HarwellXPS”, EP/Y023587/1, EP/Y023609/1, EP/Y023536/1, EP/Y023552/1 and EP/Y023544/1).

For the purpose of open access, the author has applied for a Creative Commons Attribution (CC BY) license to any Author Accepted Manuscript version arising.

Statement of originality

I confirm that this manuscript is an original paper. This manuscript, or its contents in some other form, has not been published previously, nor is it currently under consideration for publication in another journal.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.triboint.2024.110481](https://doi.org/10.1016/j.triboint.2024.110481).

Data availability

Data will be made available on request.

References

- [1] Brandon NP, Kurban Z. Clean energy and the hydrogen economy. *Philos Trans R Soc, A* 2017;375:20160400. <https://doi.org/10.1098/rsta.2016.0400>.
- [2] Dunn S. Hydrogen futures: Toward a sustainable energy system. *Int J Hydrog Energy* 2002;27:235–64. [https://doi.org/10.1016/S0360-3199\(01\)00131-8](https://doi.org/10.1016/S0360-3199(01)00131-8).
- [3] National Renewable Energy Lab. (NREL) G, CO (United States). The 1995 progress report of the secretary of energy's hydrogen technical advisory panel. US Department of Energy Office of Scientific and Technical Information 1995. <https://doi.org/10.2172/81032>.
- [4] Winter CJ. Hydrogen in high-speed air transportation. *Int J Hydrog Energy* 1990;15:579–95. [https://doi.org/10.1016/0360-3199\(80\)90006-3](https://doi.org/10.1016/0360-3199(80)90006-3).
- [5] Contreras A, Yigit S, Özyay K, Veziroğlu T. Hydrogen as aviation fuel: A comparison with hydrocarbon fuels. *Int J Hydrog Energy* 1997;22:1053–60. [https://doi.org/10.1016/S0360-3199\(97\)00008-6](https://doi.org/10.1016/S0360-3199(97)00008-6).
- [6] Cecere D, Giacomazzi E, Ingenito A. A review on hydrogen industrial aerospace applications. *Int J Hydrog Energy* 2014;39:10731–47. <https://doi.org/10.1016/j.ijhydene.2014.04.126>.
- [7] Reddi K, Elgowainy A, Sutherland E. Hydrogen refueling station compression and storage optimization with tube-trailer deliveries. *Int J Hydrog Energy* 2014;39:19169–81. <https://doi.org/10.1016/j.ijhydene.2014.09.099>.
- [8] Sawae Y, Morita T, Takeda K, Onitsuka S, Kaneuti J, Yamaguchi T, Sugimura J. Friction and wear of PTFE composites with different filler in high purity hydrogen gas. *Tribol Int* 2021;157:106884. <https://doi.org/10.1016/j.triboint.2021.106884>.
- [9] Flitney R. Seals and sealing handbook (sixth edition). Oxford: Butterworth-Heinemann; 2014.
- [10] Zhou C, Chen G, Xiao S, Hua Z, Gu C. Study on fretting behavior of rubber O-ring seal in high-pressure gaseous hydrogen. *Int J Hydrog Energy* 2019;44:22569–75. <https://doi.org/10.1016/j.ijhydene.2019.02.224>.
- [11] Ma Y, Wang XR, Li T, Zhang J, Gao J, Sun ZY. Hydrogen and ethanol: Production, storage, and transportation. *Int J Hydrog Energy* 2021;46:27330–48. <https://doi.org/10.1016/j.ijhydene.2021.06.027>.
- [12] Rossmann A. Aeroengine safety. German: Institute of Thermal Turbomachinery and Machine Dynamics. Graz University of Technology; 2023.
- [13] Committee AH. *Asm handbook committee fatigue and fracture*. United States: ASM International; 1996.
- [14] MOTION & CONTROL NSK. Damage by type: Fretting, (<https://www.nskamericas.com/en/services/troubleshooting/damage-by-type/fretting.html>); 2024 [accessed 22 October 2024].
- [15] Staffell I, Scamman D, Abad AV, Balcombe P, Dodds PE, Ekins P, Shah N, Ward KR. The role of hydrogen and fuel cells in the global energy system. *Energy Environ Sci* 2019;12:463–91. <https://doi.org/10.1039/C8EE01157E>.
- [16] Jiang L, Fu X. An ammonia-hydrogen energy roadmap for carbon neutrality: Opportunity and. *Chall China; Hydrog Knowl Cent* 2021. (<https://www.h2knowledgecentre.com/content/journal2852>).
- [17] Standard Plaoomers Pvt. bta. Technical data sheet – TDS – physical properties of PTFE and filled PTFE products (<https://www.standard-ptfe.com/pdf/data-sheet-of-ptfe.pdf>); 2023 [accessed 5th June 2023].
- [18] CPLabSafety. PTFE and Teflon chemical compatibility, (<https://www.calpacalab.com/teflon-ptfe-compatibility/>); 2024 [accessed 2024].
- [19] Balu D, Verma PC, Narala SKR, Sujith R, Saravanan P. Tribological investigation of chemically modified polytetrafluoroethylene coating for hydrogen valve application. *Tribol Lett* 2024;72:82. <https://doi.org/10.1007/s11249-024-01869-x>.
- [20] Nakashima K, Yamaguchi A, Kurono Y, Sawae Y, Murakami T, Sugimura J. Effect of high-pressure hydrogen exposure on wear of polytetrafluoroethylene sliding against stainless steel. *Proc Inst Mech Eng, Part J* 2010;224:285–92. <https://doi.org/10.1243/13506501JET642>.
- [21] Sawae Y, Yamaguchi A, Nakashima K, Murakami T, Sugimura J. Wear behavior of polymeric sealing material in gaseous hydrogen. *Int Jt Tribol Conf* 2008;43369:15–7. <https://doi.org/10.1115/1JTC2008-71225>.
- [22] Sakano Y, Iwai T, Shoukaku Y. Friction and wear properties of PTFE composites against 6061-T6 aluminium alloy under hydrogen atmosphere. *ASME/STLE Int Jt Tribol Conf* 2011 2011;54747:397–9. <https://doi.org/10.1115/1JTC2011-61258>.
- [23] Sawae Y, Nakashima K, Doi S, Murakami T, Sugimura J. Effects of high pressure hydrogen on wear of PTFE and PTFE composite. *ASME/STLE Int Jt Tribol Conf* 2009 2009;48951:233–5. <https://doi.org/10.1115/1JTC2009-15096>.
- [24] Yu K, Bayliss R, Hillman B. Wear tests of polymer composite compressor seal materials in hydrogen environments. 1999. (<https://www.osti.gov/biblio/20002653>).
- [25] Nakashima K, Morillo C, Kurono Y, Sawae Y, Sugimura J. Wear mechanisms of PTFE in humidified hydrogen gas. *Int Jt Tribol Conf* 2011;54747:229–31. <https://doi.org/10.1115/1JTC2011-61180>.
- [26] Chen Q, Morita T, Sawae Y, Fukuda K, Sugimura J. Effects of trace moisture content on tribofilm formation, friction and wear of cf-filled PTFE in hydrogen. *Tribol Int* 2023;188:108905. <https://doi.org/10.1016/j.triboint.2023.108905>.
- [27] European Chemicals Agency. Echa publishes PFAS restriction proposal, (<https://echa.europa.eu/-/echa-publishes-pfas-restriction-proposal>); 2023 [accessed 7 February 2023].
- [28] Zhang J, Wheatley A, Pasaribu R, Worthington E, Matthews S, Zinser C, Cann P. Wind turbine lubrication: Low temperature fretting wear behaviour of four commercial greases. *Tribol Int* 2023;187. <https://doi.org/10.1016/j.triboint.2023.108706>.
- [29] Bearing works. (PTFE) polytetrafluoroethylene-bearing works, (<https://www.bearingworks.com/uploaded-assets/pdfs/retainers/ptfe-datasheet.pdf>); 2016 [accessed 25 August 2016].
- [30] Kadiric A, Sayles RS, Ioannides E. Thermo-mechanical model for moving layered rough surface contacts. *J Tribology* 2008;130(1):011016. <https://doi.org/10.1115/1.2805440>.
- [31] Burriss DL, Sawyer WG. Improved wear resistance in alumina-PTFE nanocomposites with irregular shaped nanoparticles. *Wear* 2006;260:915–8. <https://doi.org/10.1016/j.wear.2005.06.009>.
- [32] Harris KL, Pitenis AA, Sawyer WG, Krick BA, Blackman GS, Kasprzak DJ, Junk CP. PTFE tribology and the role of mechanochemistry in the development of protective surface films. *Macromolecules* 2015;48:3739–45. <https://doi.org/10.1021/acs.macromol.5b00452>.
- [33] Zhou Z, Zhou Q, Qin K, Li S, Zhang K, Yuan T, Sun W. The particle breakage effect on abrasive wear process of rubber/steel seal pairs under high/low pressure. *Polymers* 2023;15:1857. <https://doi.org/10.3390/polym15081857>.
- [34] Zhang J., Bolle B., Yin S., Bera T., Wong J.S.S., Spikes H. Gaseous lubricity additives for hydrogen gas 2024 (not published Available at SSRN 4872097).

- [35] Bhaumik S, Pathak S. Effect of nano and micro friction modifier based lubricants on wear behavior between steel-steel contacts. *Tribol Ind* 2017;39:136–43.
- [36] Pitenis AA, Harris KL, Junk CP, Blackman GS, Sawyer WG, Krick BA. Ultralow wear PTFE and alumina composites: It is all about tribochemistry. *Tribol Lett* 2015;57: 1–8. <https://doi.org/10.1007/s11249-014-0445-6>.
- [37] Krick BA, Ewin JJ, McCumiskey EJ. Tribofilm formation and run-in behavior in ultra-low-wearing polytetrafluoroethylene (PTFE) and alumina nanocomposites. *Tribol Trans* 2014;57:1058–65. <https://doi.org/10.1080/10402004.2014.933934>.
- [38] Khare HS, Moore AC, Haidar DR, Gong L, Ye J, Rabolt JF, Burris DL. Interrelated effects of temperature and environment on wear and tribochemistry of an ultralow wear PTFE composite. *J Phys Chem C* 2015;119:16518–27. <https://doi.org/10.1021/acs.jpcc.5b00947>.
- [39] Shen J, Pei Y, De Hosson JTM. Structural changes in polytetrafluoroethylene molecular chains upon sliding against steel. *J Mater Sci* 2014;49:1484–93. <https://doi.org/10.1007/s10853-013-7829-0>.
- [40] Sun W, Liu X, Song Q, Liu K, Wang W, Lu Y, Ye J. Mechanochemical effect of filler surface functionality on fluoropolymer tribology. *Macromolecules* 2021;54: 6417–29. <https://doi.org/10.1021/acs.macromol.1c00395>.
- [41] Wei J, Sun W, Liu K, Liu X, Zhang K, Zhang Q, Ye J. How moisture driven mechanochemistry stabilizes transfer film adhesion and cohesion in ultralow wear PTFE composite. *Wear* 2023;516:204617. <https://doi.org/10.1016/j.wear.2022.204617>.
- [42] Thermo Fisher Scientific. Table of elements, x-ray photoelectron spectroscopy themed periodic table of elements, (<https://www.thermofisher.com/uk/en/home/materials-science/learning-center/periodic-table.html>); 2006 [accessed 2006].
- [43] Blanchet T, Kennedy F, Jayne D. Xps analysis of the effect of fillers on PTFE transfer film development in sliding contacts. *Tribol Trans* 1993;36:535–44. <https://doi.org/10.1080/10402009308983193>.
- [44] Cui W, Xu M, Tao L, Wang T, Yu C, Liang B, Ma T. In-situ observation of transfer film formation and evolution for the fabric composite lubricated spherical plain bearing at cryogenic and wide temperature range. *Appl Surf Sci* 2023;612:155946. <https://doi.org/10.1016/j.apsusc.2022.155946>.
- [45] Shi Y, Yin P, Li J, Xu X, Jiang Q, Li J, Sari HMK, Wang J, Li W, Hu J, et al. Ultra-high rate capability of in-situ anchoring FeF₃ cathode onto double-enhanced conductive Fe/graphitic carbon for high energy density lithium-ion batteries. *Nano Energy* 2023;108:108181. <https://doi.org/10.1016/j.nanoen.2023.108181>.
- [46] Bai S, Yu P, Li C, Wen S, Ding Z. Depression of pyrite in a low-alkaline medium with added calcium hypochlorite: Experiment, visual minteq models, xps, and tof-sims studies. *Min Eng* 2019;141:105853. <https://doi.org/10.1016/j.mineng.2019.105853>.
- [47] Abdel-Samad H, Watson PR. An XPS study of the adsorption of lead on goethite (α -FeOOH). *Appl Surf Sci* 1998;136:46–54. [https://doi.org/10.1016/S0169-4332\(98\)00337-7](https://doi.org/10.1016/S0169-4332(98)00337-7).
- [48] Kalegowda Y, Chan Y-L, Wei D-H, Harmer SL. X-PEEM, XPS and TOF-SIMS characterisation of xanthate induced chalcopyrite flotation: Effect of pulp potential. *Surf Sci* 2015;635:70–7. <https://doi.org/10.1016/j.susc.2014.12.012>.
- [49] Chastain J, King Jr RC. Handbook of X-Ray photoelectron spectroscopy. United States: Perkin-Elmer Corporation; 1992.
- [50] Jiang Z, Fang J, Chen B, Gu K. Effect of magnetic field on tribological performances of two lubricating oils with phosphorus-containing additives. *Lubr Sci* 2018;30: 23–32. <https://doi.org/10.1002/ls.1392>.
- [51] Theiler G, Hübner W, Gradt T, Klein P, Friedrich K. Friction and wear of PTFE composites at cryogenic temperatures11extended version of the paper presented at the 2nd world tribology congress, vienna, 3–7 september 2001. *Tribol Int* 2002;35: 449–58. [https://doi.org/10.1016/S0301-679X\(02\)00035-X](https://doi.org/10.1016/S0301-679X(02)00035-X).
- [52] Colas G, Cornuault P-H, Michel Y, Bordenave RP. Fretting wear lubrication of initially worn parts through tribo-induced anchorage of PTFE in wear scars, and tribochemical creation of graphene oxide. *Wear* 2023;524:204882. <https://doi.org/10.1016/j.wear.2023.204882>.
- [53] Zhou H, Ruther RE, Adcock J, Zhou W, Dai S, Nanda J. Controlled formation of mixed nanoscale domains of high capacity fe2o3–fe3 conversion compounds by direct fluorination. *ACS Nano* 2015;9:2530–9. <https://doi.org/10.1021/acsnano.5b00191>.
- [54] Jia C-S, Zhang L-H, Peng X-L, Luo J-X, Zhao Y-L, Liu J-Y, Guo J-J, Tang L-D. Prediction of entropy and Gibbs free energy for nitrogen. *Chem Eng Sci* 2019;202: 70–4. <https://doi.org/10.1016/j.ces.2019.03.033>.
- [55] Majzlan J, Navrotsky A, Schwertmann U. Thermodynamics of iron oxides: Part iii. Enthalpies of formation and stability of ferrihydrite ($\sim$ Fe(OH)₃), schwertmannite ($\sim$ Fe(OH)_{3/4}(SO₄)_{1/8}), and ϵ -Fe₂O₃. *Geochim Cosmochim Acta* 2004;68: 1049–59. [https://doi.org/10.1016/S0016-7037\(03\)00371-5](https://doi.org/10.1016/S0016-7037(03)00371-5).
- [56] Popovic M. Thermodynamic properties of microorganisms: Determination and analysis of enthalpy, entropy, and Gibbs free energy of biomass, cells and colonies of 32 microorganism species. *Heliyon* 2019;5:e01950. <https://doi.org/10.1016/j.heliyon.2019.e01950>.
- [57] Fan B, Xing L, Wang L, Zhang Y, Liu C, Qi X. Tribological properties of PTFE/ aramid fabric composite liner modified by PAO40/Polysulfone/SiO₂ hybrid shell microcapsules. *Tribol Trans* 2024;1–19. <https://doi.org/10.1080/10402004.2024.2368125>.
- [58] Zuo Z, Liang L, Bao Q, Yan P, Jin X, Yang Y. Molecular dynamics calculation on the adhesive interaction between the polytetrafluoroethylene transfer film and iron surface. *Front Chem* 2021;9:740447. <https://doi.org/10.3389/fchem.2021.740447>.
- [59] Ye J, Burris DL, Xie T. A review of transfer films and their role in ultra-low-wear sliding of polymers. *Lubricants* 2016;4:4. <https://doi.org/10.3390/lubricants4010004>.
- [60] Lv W, Wang T, Wang Q, Yap KK, Song F, Wang C. Tribological and mechanochemical properties of nanoparticle-filled polytetrafluoroethylene composites under different loads. *Polymers* 2024;16:894. <https://doi.org/10.3390/polym16070894>.